AN INVESTIGATION OF THE PHOTOCHEMICAL AND EXCITED STATE PROPERTIES OF SELECTED SECOND AND THIRD ROW TRANSITION METAL COMPLEXES

Thesis by

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ABSTRACT

The photochemical properties of several different types of 2nd and 3rd row transition metal complexes are discussed. Complexes of the type $[M(CN)_5X]^{n-}$ $[M = Rh(III), Ir(III); X = Cl^-, Br^-, I^-, H_2O, OH^-, NCCH_3]$ have been prepared and characterized by electronic and infrared absorption spectral measurements. The complexes are readily prepared by thermal anation reactions of $[M(CN)_5H_2O]^{2-}$, the aquo complexes being formed by uv irradiation of acidic solutions of $[M(CN)_6]^{3-}$. The lowest energy electronic absorption band in the $[Rh(CN)_5X]^{n-}$ complexes is assigned to the ligand field transition ${}^1A_1 \rightarrow {}^1E^a$, whereas in $[Ir(CN)_5X]^{n-}$ both ${}^1A_1 \rightarrow {}^3E^a$ and ${}^1A_1 \rightarrow {}^1E^a$ absorptions are observed. The position of the ${}^1A_1 \rightarrow {}^1E^a$ transition establishes the order of decreasing ligand field strength of X as $NCCH_3 > OH^- > H_2O > Cl^- > Br^- > I^-$ for both Rh(III) and Ir(III) complexes. Halide-to-metal charge transfer bands are observed for $[M(CN)_5X]^{n-}$ complexes with $X = Br^-$ and I^-.

Ultraviolet irradiation of H_2 and O_2 adducts of $IrCl(CO)(PPh_3)_2$, $IrI(CO)(PPh_3)_2$, $[Ir(2\text{-phos})_2]^+$, and $[Ir(2{=}\text{phos})_2]^+$ has been found to induce reductive-elimination of molecular hydrogen and oxygen and regeneration of the square-planar complexes. The reactions occur in argon purged solutions and in frozen EPA solutions of the adducts at 77°K.

Absorption and emission spectra for the square planar complexes $[Rh(2\text{-phos})_2]Cl$, $[Rh(2{=}\text{phos})_2]Cl$, $[Ir(2\text{-phos})_2]Cl$, and

[Ir(2=phos)$_2$]Cl (2-phos is 1,2-bis(diphenylphosphino)ethane; 2=phos is *cis*-1,2-bis(diphenylphosphino)ethylene) have been measured in the solid state and in frozen EPA [ethyl ether-isopentane-ethyl alcohol (5:5:2)] solution at 77 °K. Of the four complexes, only [Rh(2=phos)$_2$]Cl fails to luminesce in the solid state at room temperature. At 77 °K in EPA the emission maxima fall in the range 16.8-18.4 kcm^{-1}, and the emission lifetimes are between 8.2 and 20.8 μsec; [Ir(2=phos)$_2$]Cl exhibits an unusually sharp, strongly overlapping emission/absorption system, with an emission quantum yield of 0.93 ± 0.07. It is suggested that in the Ir(I) cases emission occurs from a square planar $\underline{d}^{7}\,a_{2u}$ charge transfer state of E_u ($^3A_{2u}$) symmetry. The fact that the emission maxima of the two Rh(I) complexes are both red-shifted by about 4000 cm^{-1} from the lowest absorption peak is discussed in terms of an admixture of ligand field character in the primarily $\underline{d}^{7}\,a_{2u}$ emitting state, which could give rise to a distortion of the RhP$_4$ core towards tetrahedral geometry. The absorption and emission spectra of several other Rh(I) complexes are also briefly discussed.

Irradiation of [(*n*-C_4H_9)$_4$N]$_2$[Re_2Cl_8], **1**, in CH_3CN results in cleavage of the Re_2 quadruple bond and formation of monomeric Re(III) products. The primary photoproduct is [$ReCl_4(CH_3CN)_2$]$^-$, **2**, and this species can be further photolyzed in CH_3CN to give $ReCl_3$-$(CH_3CN)_3$, **3**. The quantum yield of disappearance of **1** upon irradiation at 313 nm was found to be 0.017 ± 0.005. **2** is also the primary

photoproduct under 254 nm irradiation. Irradiation of $\underset{\frown}{1}$ in CH_3CN with a He-Ne laser (632.8 nm) does not lead to reaction, indicating that the excited state derived from the $\delta \rightarrow \delta^*$ transition is not photoactive. Cleavage of the Re_2 unit is observed, however, when solutions are irradiated at 366 nm.

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CHAPTER I

Preparation, Spectral Studies, and Photochemical Properties of Hexacyano- and Acidopentacyanorhodate(III) and -Iridate(III) Complexes

Introduction

A comparison of the spectral and chemical properties of metal complexes with identical ligands but different transition metals of the same column in the periodic table can give much information about the nature of ground state electronic structures and fine details of metal-ligand bonding. If photochemical properties are included in such comparisons, one can also infer information about the nature of excited states in the complexes. To date, the photochemical reactions of only two series of complexes have been examined in sufficient detail to allow such comparisons. The first of these is the Group VIB metal carbonyls, $M(CO)_6$ and $M(CO)_5L$ (M = Cr(0), Mo(0), W(0)), for which the photochemistry has been extensively reviewed by several authors.[1-3] In the presence of excess ligand L, the three metal hexacarbonyls show parallel photochemistry with each substituting L for CO with a quantum yield of 1. The $M(CO)_5L$ complexes, however, show similar, but not identical, photochemistry, and differences in photochemical properties have led to many inferences about the nature of the bonding in the excited states.

The second series of compounds for which significant comparisons can be made is the amine complexes of the Group VIII metals, Co(III), Rh(III), and Ir(III). In contrast to the Group VI B metal carbonyls, there exists a wide disparity in the photochemical properties of these Group VIII complexes. The cobalt amines generally show very low quantum yield or no photochemistry when irradiated into lower energy ligand field (LF) bands, and reduction to Co(II) when irradiation is into charge transfer (CT) bands.[2] The only identified exception to this is $[Co(NH_3)_5N_3]^{2+}$, which gives NH_3 release and formation of $[Co(NH_3)_4H_2O(N_3)]^{2+}$, with $\phi = 0.20$ with 19.2 kcm^{-1} LF irradiation.[4] In contrast, LF irradiation of Rh(III) amine complexes generally leads to efficient substitution chemistry.[5-7] Charge transfer irradiation of rhodium amines commonly gives redox chemistry and transient generation of Rh(II) species.[8-11] Unfortunately, very little work has been done with iridium amines.[10] The differences in the photochemical properties of the Co(III) amines as compared to the analogous Rh(III) complexes, and fine differences between members of a series of $[Rh(NH_3)_5X]^{n+}$ complexes have sparked a great deal of interest and research into the properties of these types of compounds.[5-11]

In contrast to the photoinduced redox behavior of Co(III) amines, cyanide complexes of Co(III) generally show clean and moderately efficient photosubstitution chemistry.[2] The photochemical reactions of $[Co(CN)_6]^{3-}$, a large variety of $[Co(CN)_5X]^{n-}$ complexes, and a few $[Co(CN)_4X_2]^{n-}$ and $[Co(CN)_4(X)Y]^{n-}$ complexes have been extensively investigated in recent years.[2,12-18] However, prior to this study, not a single report had appeared concerning the photochemical properties of Rh(III) and Ir(III) cyanide complexes, and surprisingly, only a few pentacyanorhodate(III) and -iridate(III) derivatives were known. This investigation into the photochemical properties of rhodium and iridium cyanide complexes was thus initiated with the aim of comparing observed properties to those of analogous cobalt species.

Before proceeding to the results of this investigation, it is appropriate here to briefly review the known photochemistry of cobalt cyanide complexes. Irradiation of $[Co(CN)_6]^{3-}$ in acidic solution has been shown to result in aquation (Eq. 1):

$$[Co(CN)_6]^{3-} \xrightarrow[H_2O]{h\nu} [Co(CN)_5H_2O]^{2-} + CN^- \qquad (1)$$

Conversion to the aquo complex can be made to go to completion, and the quantum yield of aquation is 0.31 at 25 °C and is independent of irradiation wavelength.[14] Irradiation of $[Co(CN)_5H_2O]^{2-}$ in neutral or acidic solutions leads primarily to water exchange,[2] and it has recently been found that loss of CN^- occurs with very low efficiency to give a diaquo species.[15] Irradiation of $[Co(CN)_6]^{3-}$ in alkaline solution results in initial formation of $[Co(CN)_5OH]^{3-}$, and photolysis of $[Co(CN)_5OH]^{3-}$ in basic media causes release of CN^- and formation of $[Co(CN)_4(OH)_2]^{3-}$. Conversion to $[Co(CN)_4(OH)_2]^{3-}$ can be as high as 90%.[15] Irradiation of $[Co(CN)_6]^{3-}$ and $[Co(CN)_5H_2O]^{2-}$ in the presence of anating agents such as N_3^-, SCN^-, or I^- has been reported to lead to the corresponding acidopentacyanocobaltate(III) complex,[16,17] apparently proceeding through $[Co(CN)_5H_2O]^{2-}$ in the case of $[Co(CN)_6]^{3-}$.[17]

Acidopentacyanocobaltate(III) complexes are normally prepared by the Co(II) catalyzed action of cyanide on $[Co(NH_3)_5X]^{n+}$, or by the action of an appropriate oxidizing agent on $[Co(CN)_5]^{3-}$.[19] For example, $[Co(CN)_5Br]^{3-}$ can be prepared by either of the following reactions:

$$Co^{II} + 5CN^- + [Co(NH_3)_5Br]^{2+} \rightarrow [Co(CN)_5Br]^{3-} + Co^{II} + 5NH_3 \tag{2}$$

$$[Co(CN)_5]^{3-} + \tfrac{1}{2}Br_2 \rightarrow [Co(CN)_5Br]^{3-} \tag{3}$$

However, neither method gives an analytically pure product. The first reaction (Eq. 2) is thought to occur by an inner sphere redox process (Eqs. 4-6)[19]:

$$Co^{II} + 5CN^- \rightarrow [Co(CN)_5]^{3-} \tag{4}$$

$$[Co(CN)_5]^{3-} + [Co(NH_3)_5X]^{2+} \rightarrow [Co(CN)_5X]^{3-} + [Co(NH_3)_5]^{2+} \tag{5}$$

$$[Co(NH_3)_5]^{2+} \rightarrow Co^{II} + 5NH_3 \tag{6}$$

A large number of $[Co(CN)_5X]^{n-}$ complexes have been prepared, and the ligand X can be Cl^-, Br^-, I^-, SCN^-, NCS^-, H_2O, OH^-, N_3^-, SO_3^{2-}, $NCCH_3$, $NCSe^-$, H^-, benzyl$^-$, and $C_2F_4H^-$.[19] The photochemical properties of many of these complexes have been investigated and the principal photoreaction is aquation of X.[2,12,13,16] Irradiation of aqueous solutions of $[Co(CN)_5X]^{3-}$ ($X = Cl^-$, Br^-, I^-), for example, leads to formation of $[Co(CN)_5H_2O]^{2-}$. The quantum yield of aquation varies with the ligand X, but appears to be independent of irradiation wavelength for a given X, as shown in Table I-1.[7]

Table I-1: Quantum Yield of Aquation of $[Co(CN)_5X]^{n-}$ Complexes.[7]

Complex	Excitation (nm)	Type of Excitation	Quantum Yield	Remarks
$[Co(CN)_6]^{3-}$	254	LF[a]	0.31	25°, pH 2-7.5
	313	LF	0.31	25°, pH 2-7.5
	365	LF	0.31	25°, pH 2-7.5
$[Co(CN)_5Cl]^{3-}$	370	LF	0.06	natural pH
$[Co(CN)_5Br]^{3-}$	370	LF	0.17	natural pH
$[Co(CN)_5I]^{3-}$	380	CT[a]	0.17	25°, natural pH
	500	LF	0.17	25°, natural pH

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[a] LF = ligand field, CT = charge transfer.

The mechanism of photosubstitution of $[Co(CN)_6]^{3-}$ is different from that for $[Co(CN)_5X]^{n-}$. Recent results suggest that photoaquation of $[Co(CN)_6]^{3-}$ proceeds via an associative mechanism with substitution of an inner sphere CN^- by an outer sphere H_2O[17]:

$$[Co(CN)_6]^{3-}(H_2O)_n \xrightarrow{h\nu} [Co(CN)_6]^{3-}(H_2O)_n^{*} \qquad (7)$$

$$[Co(CN)_6]^{3-}(H_2O)_n^{*} \longrightarrow [Co(CN)_5H_2O]^{2-}(CN^-)(H_2O)_{n-1} \qquad (8)$$

However, this work conflicts with results reported earlier in the literature by other authors.[16] Photosubstitution of $[Co(CN)_5X]^{n-}$ ($X = H_2O$, Cl^-, Br^-, I^-) proceeds via a dissociative mechanism yielding a five coordinate intermediate that subsequently reacts with the anating ligand Y[16,17]:

$$[Co(CN)_5X]^{n-} \xrightarrow{h\nu} [Co(CN)_5]^{2-} + X \qquad (9)$$

$$[Co(CN)_5]^{2-} + Y \longrightarrow [Co(CN)_5Y]^{n-} \qquad (10)$$

Thermal anation reactions of $[Co(CN)_5H_2O]^{2-}$ in the presence of an excess of anating ligand are also thought to proceed via a dissociative mechanism.[20]

Although $[Rh(CN)_6]^{3-}$ and $[Ir(CN)_6]^{3-}$ have been known for many years,[19] the only pentacyanorhodate(III) and -iridate(III) derivatives reported to date have been $[Rh(CN)_5C_2F_4H]^{3-}$,[21] $[Rh(CN)_5NO_2]^{3-}$,[21] $[Rh(CN)_5COCH_3]^{3-}$,[22] $[Rh(CN)_5H]^{3-}$,[22] and $[Ir(CN)_5H]^{3-}$,[23] and these were prepared by very indirect methods. The scarcity of these $[M(CN)_5X]^{n-}$ (M = Rh(III), Ir(III)) derivatives, and notably the lack of any halide complexes, can be attributed to the inability of rhodium and iridium to form stable $[Rh^{II}(CN)_5]^{3-}$ and $[Ir^{II}(CN)_5]^{3-}$ complexes.[19] Consequently, the reactions in Equations 2-3 do not occur for these metals, and prior to this study alternate preparative methods had not been found.

Experimental

Purification of $K_3[Rh(CN)_6]$ and $K_3[Ir(CN)_6]$. The starting chemicals for all the photochemical studies and preparations, $K_3[Rh(CN)_6]$ and $K_3[Ir(CN)_6]$, were obtained from Varlacoid Chemical Company, Elizabeth, New Jersey. The purity of these compounds as supplied varied from sample to sample, and although infrared evidence indicated that a few samples of relatively pure $K_3[Ir(CN)_6]$ were obtained, samples of $K_3[Rh(CN)_6]$ always contained a significant amount (5-10%) of impurity. This impurity, which showed infrared bands between 1200 and 1500 cm^{-1} and at 620 cm^{-1}, was never identified but most likely was an oxidation product of the original compound and possibly a cyanorhodium-carboxylate or -cyanate complex. $H_3[Co(CN)_6]$ is known to undergo oxidation to give $[Co(CN)_5(HCO_2)]^{3-}$.[24] Attempts at recrystallizing $K_3[Rh(CN)_6]$ from water-alcohol solutions did not improve the purity but actually appeared to decrease it. The best purification procedure was found to be chromatography of the compound, first on alumina, and then on silica gel, with water as the eluent. In each case the first and last fractions were discarded. After the solutions were concentrated and added to a large excess of acetone, the resultant precipitate was collected, washed with acetone and dried over P_2O_5 under vacuum. This process was repeated until infrared spectra showed negligible amounts of impurities. This procedure was used for obtaining samples for measurement of the absorption spectra of $[Rh(CN)_6]^{3-}$, $[Ir(CN)_6]^{3-}$, $[Rh(CN)_5H_2O]^{2-}$, and $[Ir(CN)_5H_2O]^{2-}$. For all other irradiations, the compounds were used as supplied without further purification.

Irradiation of Solutions. All irradiations were conducted in a hood using either quartz (1 cm path length) cells, or 20 or 100 ml quartz beakers, using an Ultraviolet Products lamp with principal output at 254 nm (43.3 kcm^{-1}). Samples were cooled with a forced air stream. Solutions were either buffered at pH 6 with K_2HPO_4/KH_2PO_4, acidified to pH 1.5 - 3.0 with $HClO_4$, left unbuffered (pH 9 - 10 for $[M(CN)_6]^{3-}$), or made alkaline to pH 12 - 13 with KOH.

$[Rh(CN)_5H_2O]^{2-}$ and $[Ir(CN)_5H_2O]^{2-}$. Acidic or pH 6 buffered solutions were irradiated until the absorption band corresponding to $[M(CN)_5H_2O]^{2-}$ reached a maximum value. This required approximately 3h for a 10^{-3} M $K_3[Rh(CN)_6]$ solution and 95h for a 10^{-3} M $K_3[Ir(CN)_6]$ solution. All attempts to isolate the $[M(CN)_5H_2O]^{2-}$ complexes from aqueous solution were unsuccessful. The irradiated solutions showed no absorption changes after being stored in the dark for several months. Band maxima and extinction coefficients for $[Rh(CN)_5H_2O]^{2-}$ and $[Ir(CN)_5H_2O]^{2-}$ were determined by irradiating a carefully prepared, pH 6 buffered solution of the corresponding $[M(CN)_6]^{3-}$ complex until the absorption spectra showed no further changes with continued irradiation. Only one detectable band eluted when these solutions were chromatographed on silica gel or alumina.

$K_3[Rh(CN)_5I]$ and $K_3[Ir(CN)_5I]$. A solution containing 0.2 g of $K_3[Rh(CN)_6]$ or $K_3[Ir(CN)_6]$ in 20 ml of aqueous $HClO_4$ with an initial pH of 2 was irradiated until the absorption band corresponding to $[M(CN)_5H_2O]^{2-}$ reached a maximum. The solution was then brought to pH 7 with KOH, concentrated by evaporation to a volume of about 2 ml, and cooled in an ice bath. The solution was then decanted from the $KClO_4$ precipitate and a large (~100 fold) excess of KI was added, after which the reaction mixture was left in the dark for 24h. The 2 ml solution was then poured into 150 ml of acetone, and the resultant precipitate collected and washed with acetone and with methanol. Elemental analyses on these and the other $K_n[M(CN)_5X]$ compounds reported herein showed a significant amount of the anating agent KX present. Repeated attempts at removing the KX were unsuccessful. However, satisfactory analyses for several $[Co(NH_3)_6]^{3+}$ salts, as outlined below, were obtained.

$[Co(NH_3)_6][Rh(CN)_5I]$ and $[Co(NH_3)_6][Ir(CN)_5I]$. The $K_3[M(CN)_5I]$ salts from above were dissolved in a small amount of water (~2 ml), filtered, and then added to a saturated aqueous solution of $[Co(NH_3)_6]Cl_3$ (Anal. Calcd: Co, 22.03; N, 31.41; H, 6.73; Cl, 39.83. Found: Co, 21.82; N, 31.53; H, 7.01; Cl, 39.70). The solution was stirred and placed in an ice bath for two hours after which the resultant yellow crystals were filtered, washed with cold water, and dried over P_2O_5. Anal. Calcd for $[Co(NH_3)_6][Rh(CN)_5I]$: Co, 11.31; N, 29.56; Rh, 19.75; C, 11.52; I, 24.36. Found: Co, 11.10; N, 29.43; Rh, 20.24; C, 11.88; I, 24.32. Calcd for

$[Co(NH_3)_6][Ir(CN)_5I]$: Co, 9.66; N, 25.24; Ir, 31.51; C, 9.84; I, 20.80. Found: Co, 10.22; N, 25.59; Ir, 32.01; C, 10.94; I, 20.42.

$K_3[Rh(CN)_5Br]$, $K_3[Ir(CN)_5Br]$, $K_3[Rh(CN)_5Cl]$, $K_3[Ir(CN)_5Cl]$, $K_3[Rh(CN)_5SCN]$, and $K_3[Ir(CN)_5SCN]$. Preparation of these complexes was similar to the method used to make the iodo complexes, except that KBr, LiCl, and KSCN were used in the anation reaction. $[Ir(CN)_5H_2O]^{2-}$ reacts very slowly with Cl^- at room temperature, so the conversion was carried out for 48h at 60 °C.

$[Co(NH_3)_6][Rh(CN)_5Br]$, $[Co(NH_3)_6][Ir(CN)_5Br]$, $[Co(NH_3)_6]$-$[Rh(CN)_5Cl]$, and $[Co(NH_3)_6][Ir(CN)_5Cl]$. These complexes were prepared in a manner similar to that used for the iodo complexes. Anal. Calcd for $[Co(NH_3)_6][Ir(CN)_5Br]$: Co, 10.47; N, 27.35; Ir, 34.14; C, 10.66; Br, 14.19. Found: Co, 10.63; N, 28.68; Ir, 34.91; C, 11.72; Br, 12.13. Calcd for $[Co(NH_3)_6][Rh(CN)_5Br]$: Co, 12.44; N, 32.51; Rh, 21.72; C, 12.67; Br, 16.87. Found: Co, 12.17; N, 32.65; Rh, 21.70; C, 12.62; Br, 16.81. Calcd for $[Co(NH_3)_6][Ir(CN)_5Cl]$: Co, 11.36; N, 29.70; Ir, 37.06; C, 11.57; Cl, 6.84. Found: Co, 10.88; N, 29.89; Ir, 37.07; C, 11.57; Cl, 6.80.

$K_2[Rh(CN)_5NCCH_3]$ and $K_2[Ir(CN)_5NCCH_3]$. Preparation of these complexes was similar to the method used to make the iodo complexes, except that 10 ml of acetonitrile was added to the 2 ml aqueous solution of $[M(CN)_5H_2O]^{2-}$. The aqueous acetonitrile solution was either left in the dark for 24h or was irradiated for 1h at 254 nm

(39.4 $\mathrm{kcm^{-1}}$) and then allowed to stand for 4h. In either case conversion to $[\mathrm{M(CN)_5NCCH_3}]^{2-}$ was found to be essentially complete. The solution was then concentrated to a volume of about 2 ml and poured slowly into 150 ml of acetone. The resultant precipitate was collected, washed with acetone, and dried over P_2O_5. Attempts at preparing $[\mathrm{Co(NH_3)_5Cl}][\mathrm{M(CN)_5NCCH_3}]$ salts were unsuccessful and satisfactory analyses were not obtained for $\mathrm{K_2}[\mathrm{M(CN)_5NCCH_3}]$. The ir and uv spectral data, however, are consistent with the formulation $[\mathrm{M(CN)_5NCCH_3}]^{2-}$ for the anions.

$[\mathrm{Rh(CN)_5OH}]^{3-}$ and $[\mathrm{Ir(CN)_5OH}]^{3-}$. Solutions containing $[\mathrm{M(CN)_5H_2O}]^{2-}$ were made alkaline to pH 12 by addition of KOH. By monitoring the uv spectral changes during the addition of base, titration curves for the coordinated water were obtained. At pH 12 conversion to $[\mathrm{M(CN)_5OH}]^{3-}$ is essentially complete. All attempts to isolate solid salts of the hydroxo complexes were unsuccessful.

Attempted Preparation of $[\mathrm{Rh(CN)_4I_2}]^{3-}$. An acidic solution of $[\mathrm{Rh(CN)_6}]^{3-}$ was irradiated at 254 nm (43.3 $\mathrm{kcm^{-1}}$) until the $[\mathrm{Rh(CN)_5H_2O}]^{2-}$ band at 37.7 $\mathrm{kcm^{-1}}$ reached maximum absorbance. The solution was then made alkaline to pH 12 with KOH, and irradiation was continued until no further spectral changes occurred (~ 8h). The principal component of the solution then was $[\mathrm{Rh(CN)_4(OH)_2}]^{3-}$. The solution was brought to pH 7, and a 10-fold excess of KI added. The solution turned yellow after sitting overnight, and concentration and addition of the solution to acetone gave a yellow precipitate. No attempt was made to characterize the precipitate.

Spectral Measurements. Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer using KBr pellets prepared from ir spectrograde KBr powder (MC and B). Electronic absorption spectra were measured using a Cary 17 spectrophotometer. Spectra at liquid nitrogen temperature were obtained using a low temperature dewar fitted with Suprasil quartz windows, and modified to hold a standard 1.00 cm cell. A solution prepared by mixing equal volumes of saturated aqueous LiCl and water was used for low temperature glasses. The 77°K spectra were not corrected for solvent contraction.

Results and Discussion

Photolysis of $K_3[Rh(CN)_6]$ and $K_3[Ir(CN)_6]$. Irradiation of neutral or acidic solutions of $K_3[Rh(CN)_6]$ and $K_3[Ir(CN)_6]$ results in the spectral changes shown in Figure I-1. As the photolysis of $[Rh(CN)_6]^{3-}$ proceeds, a new band grows in at 37.7 kcm^{-1}, and with $[Ir(CN)_6]^{3-}$, new absorption features appear at 37.0 and 42.6 kcm^{-1}. The new absorption bands maximize with continued irradiation and then slowly decrease in intensity with very prolonged photolysis. Attempts at isolating an analytically pure solid product from these solutions have been unsuccessful. Contamination from the buffer or salt of the acid used to control the pH during the irradiation is a problem, and solid samples that were obtained showed infrared features similar to that of the impurity in purchased samples of $K_3Rh(CN)_6$. These features become more prominent the longer the solid samples are left in air. Evidence presented below strongly indicates that the

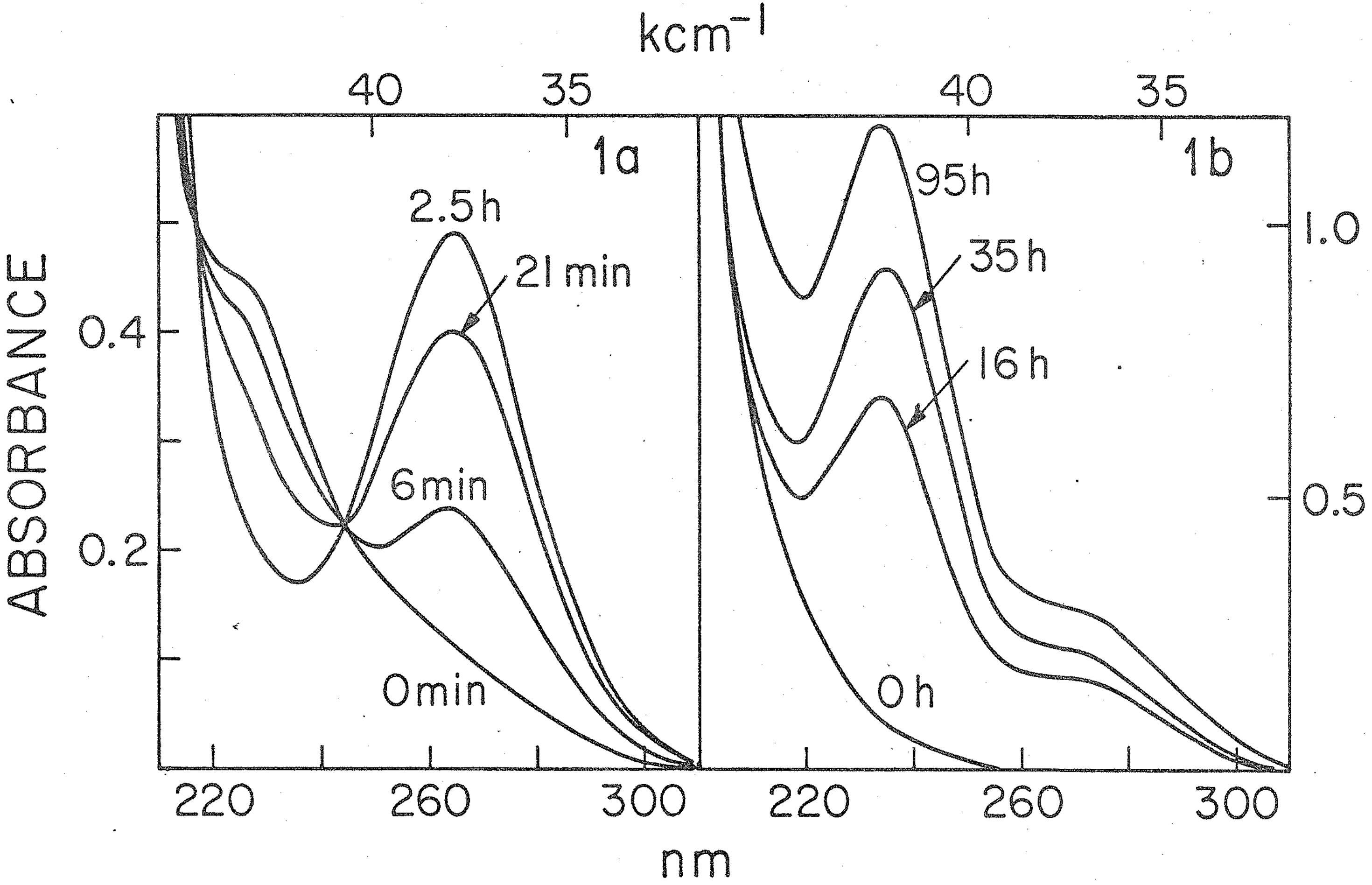


Figure I-1. Spectral changes during 254 nm (39.4 kcm^{-1}) irradiation of pH 6 buffered solutions: a, 8.1 × 10^{-4} M $K_3[Rh(CN)_6]$; b, 1.5 × 10^{-3} M $K_3[Ir(CN)_6]$.

primary photoproduct, and that which accounts for the final spectral features in Figure I-1, is in each case a $[M(CN)_5H_2O]^{2-}$ species, and it appears that these aquo complexes are very sensitive to decomposition in the solid state. This is not surprising, for although pure $K_2[Co(CN)_5H_2O]$ can be obtained by careful precipitation and recrystallization procedures,[25] and solid $Ag_2[Co(CN)_5H_2O]$ has been isolated,[26] both compounds undergo loss of H_2O upon standing or heating to give an unknown polymeric form of $[Co(CN)_5]^{2-}$.[25,26] It is thus unlikely that any solid $[Rh(CN)_5H_2O]^{2-}$ or $[Ir(CN)_5H_2O]^{2-}$ can be isolated and stored for any length of time without decomposition.

Although analyzed products have not been obtained, by analogy to the known photochemistry of $[Co(CN)_6]^{3-}$, irradiation of $[Rh(CN)_6]^{3-}$ and $[Ir(CN)_6]^{3-}$ almost certainly produces the corresponding pentacyanoaquo derivative. Strong support of this assertion comes from measurement of pH changes during the irradiation (Figure I-2), indicating loss of 1.0 ± 0.02 cyanide from $[M(CN)_6]^{3-}$,[27] and, as shown later, analytically pure samples of $[M(CN)_5X]^{n-}$ derivatives can be prepared from solutions of the photolysis product. Furthermore, the photochemical properties of the $[M(CN)_5X]^{n-}$ ($M = Rh(III)$, $Ir(III)$) derivatives, in analogy to the known photochemistry of $[Co(CN)_5X]^{n-}$ complexes, indicate that $[M(CN)_5H_2O]^{2-}$ is formed upon irradiation, and the absorption spectra of these aquo species are identical to the final spectra shown in Figure I-1. Finally, the spectral data presented later in this chapter support the conclusion that $[Rh(CN)_5H_2O]^{2-}$ and $[Ir(CN)_5H_2O]^{2-}$ are the primary products of the photolysis (Eq. 11):

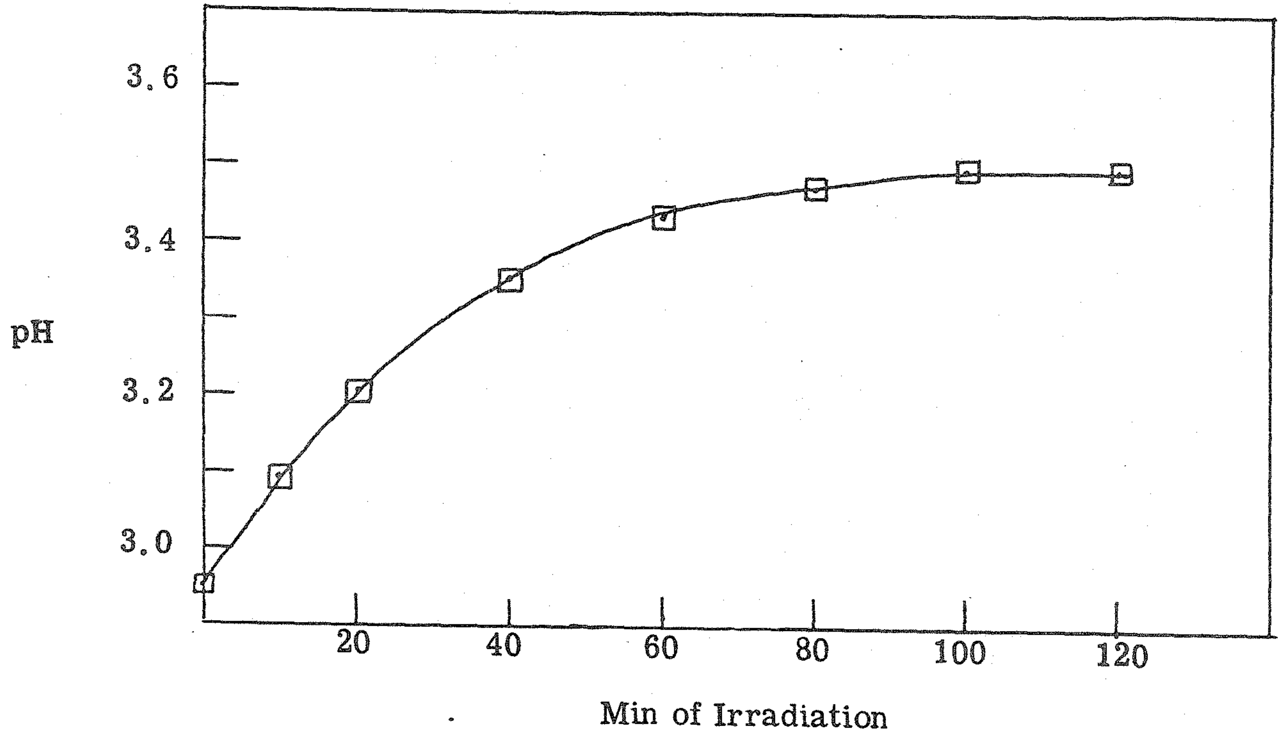


Figure I-2. pH changes during 254 nm photolysis of $K_3[Rh(CN)_6]$.

$$[M(CN)_6]^{3-} \text{ (M = Rh(III), Ir(III)} \xrightarrow[H_2O]{h\nu} [M(CN)_5H_2O]^{2-} + CN^- \qquad (11)$$

The aquo complexes can be titrated by KOH and the reaction that occurs is conversion of coordinated water to hydroxide (Eq. 12):

$$[M(CN)_5H_2O]^{2-} + OH^- \rightarrow [M(CN)_5OH]^{3-} + H_2O \qquad (12)$$

The spectral changes that occur during titration of $[Ir(CN)_5H_2O]^{2-}$ are shown in Figure I-3. A plot of pH versus absorbance at 43.5 kcm^{-1} for $[Rh(CN)_5H_2O]^{2-}$ and at 42.6 kcm^{-1} for $[Ir(CN)_5H_2O]^{2-}$ gives a titration curve from which pKa values of the coordinated water can be obtained. The plot for $[Ir(CN)_5H_2O]^{2-}$ is shown in Figure I-4, and the pKa for $[Rh(CN)_5H_2O]^{2-}$ is 10.4 and for $[Ir(CN)_5H_2O]^{2-}$ is 9.8. These compare favorably with the value of 9.7 for $[Co(CN)_5H_2O]^{2-}$.[28]

Irradiation of $[Rh(CN)_6]^{3-}$ in pH 12 solution gives the spectral changes shown in Figure I-5. A band at 38.5 kcm^{-1} grows in very rapidly but then loses intensity as a second band grows in at 31.3 kcm^{-1}. The 38.5 kcm^{-1} band is at the same position as the principal absorption feature of $[Rh(CN)_5OH]^{3-}$, and hence this initial photoreaction is most likely formation of the hydroxo complex (Eq. 13):

$$[Rh(CN)_6]^{3-} \xrightarrow[OH^-]{h\nu} [Rh(CN)_5OH]^{3-} + CN^- \qquad (13)$$

It is apparent from the spectral changes that $[Rh(CN)_5OH]^{3-}$ is itself photoactive under the conditions of the experiment and is converted to other products. A similar reactivity pattern obtains for photolysis of $[Ir(CN)_6]^{3-}$ in basic media.

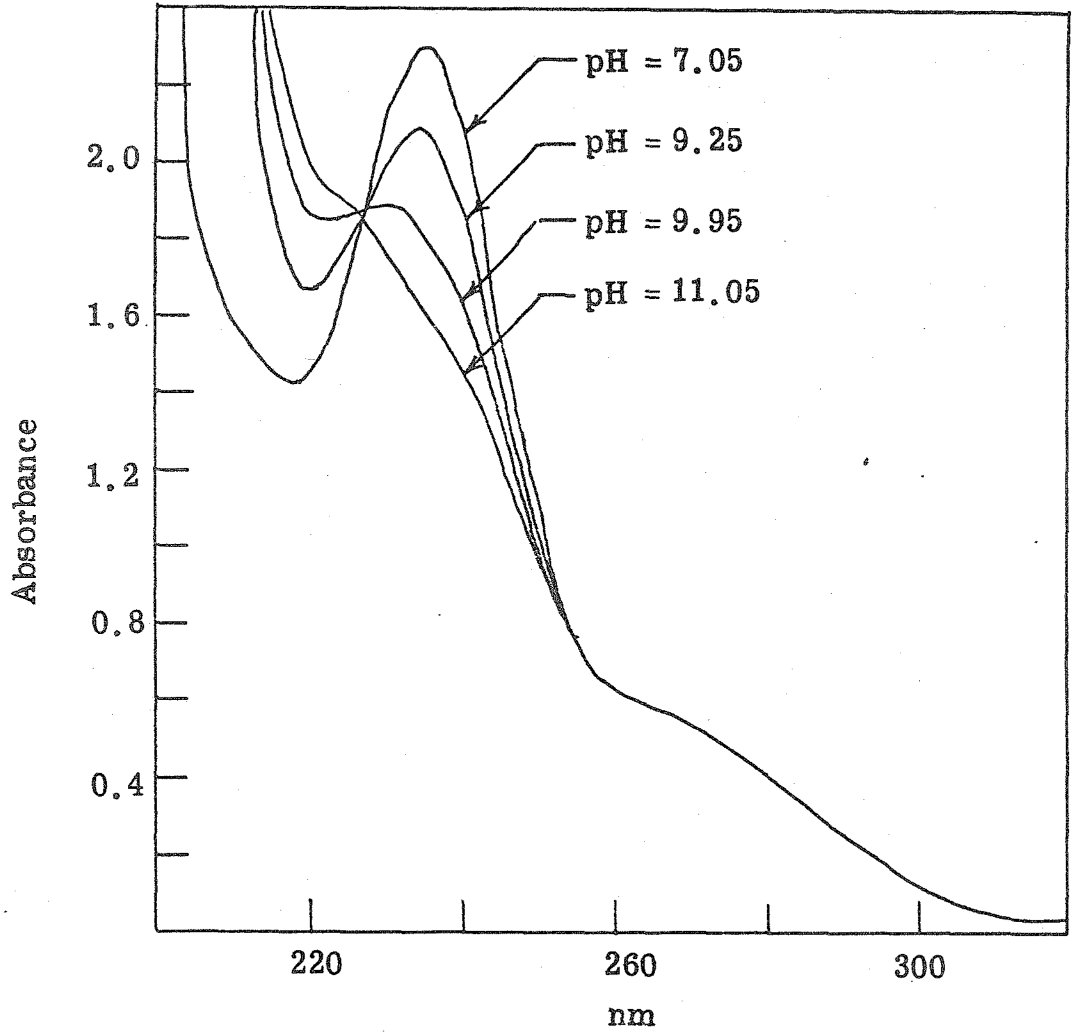


Figure I-3. Electronic spectra of $K_2[Ir(CN)_5H_2O]$ at various pH values.

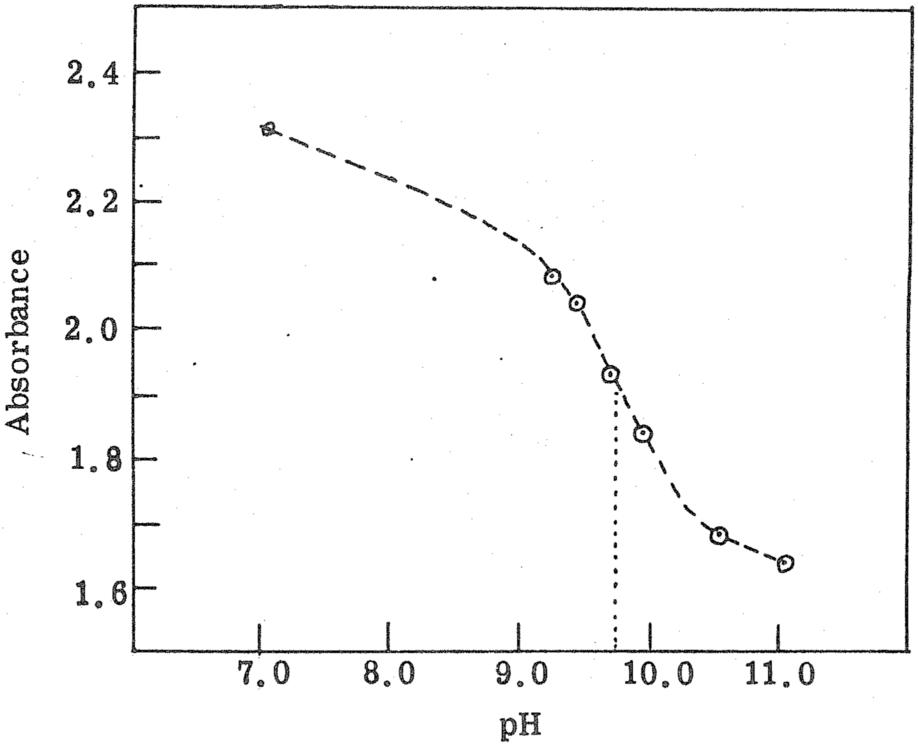


Figure I-4. Absorbance at 235 nm versus pH for [Ir $(CN)_5OH_2]^{2-}$ in aqueous solution.

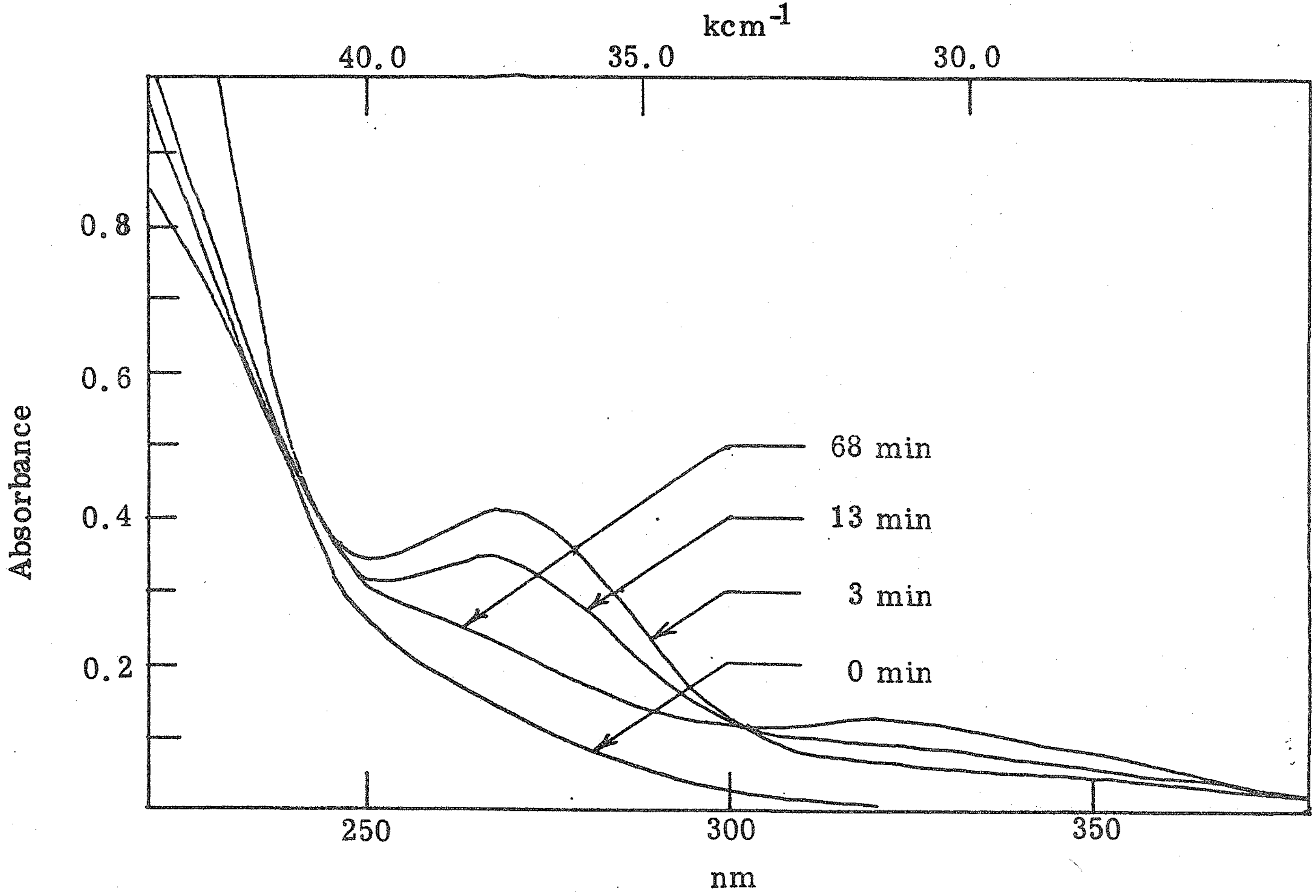


Figure I-5. Spectral changes during 254 nm irradiation of a pH 12 solution of $K_3[Rh(CN)_6]$.

Preparation of $[M(CN)_5X]^{n-}$ Derivatives. Addition of a large excess of ligand X to a solution of photochemically prepared $[M(CN)_5H_2O]^{2-}$ (M = Rh(III), Ir(III)), results in substitution of X for H_2O and formation of $[M(CN)_5X]^{n-}$ (Eq. 14):

$$[M(CN)_5H_2O]^{2-} + X \rightarrow [M(CN)_5X]^{n-} + H_2O \tag{14}$$

This provides a convenient synthetic route for otherwise unattainable $[M(CN)_5X]^{n-}$ derivatives and to date has been observed for X = Cl^-, Br^-, I^-, $NCCH_3$, SCN^-, N_3^-,[29] and NO_2^-.[29] These thermal anation reactions can be followed spectrally, and Figure I-6 shows the spectral changes that occur during the formation of $[Rh(CN)_5Br]^{3-}$. The presence of the isosbestic points is consistent with a smooth conversion to a single product.

A great deal of difficulty is encountered in obtaining analytically pure potassium salts of the derivatives, as contamination by the anating agent is inevitably present. However, analyzed samples of the Cl^-, Br^-, and I^- derivatives are obtainable as $[Co(NH_3)_6]^{3+}$ salts. Addition of this large cation to aqueous solutions of $[M(CN)_5X]^{n-}$ causes precipitation of the mixed $[Co(NH_3)_6][M(CN)_5X]$ salts, and the anating agent and other impurities are left in solution. These mixed salts are only slightly soluble in water and are not very useful except for analysis. The ir and uv absorption features of the $[Co(NH_3)_6]^{3+}$ ion preclude a detailed spectroscopic study of the mixed salts, but the features of the $[M(CN)_5X]^{3-}$ ions are nevertheless discernible in the spectra, indicating that the same $[M(CN)_5X]^{3-}$ species is present in

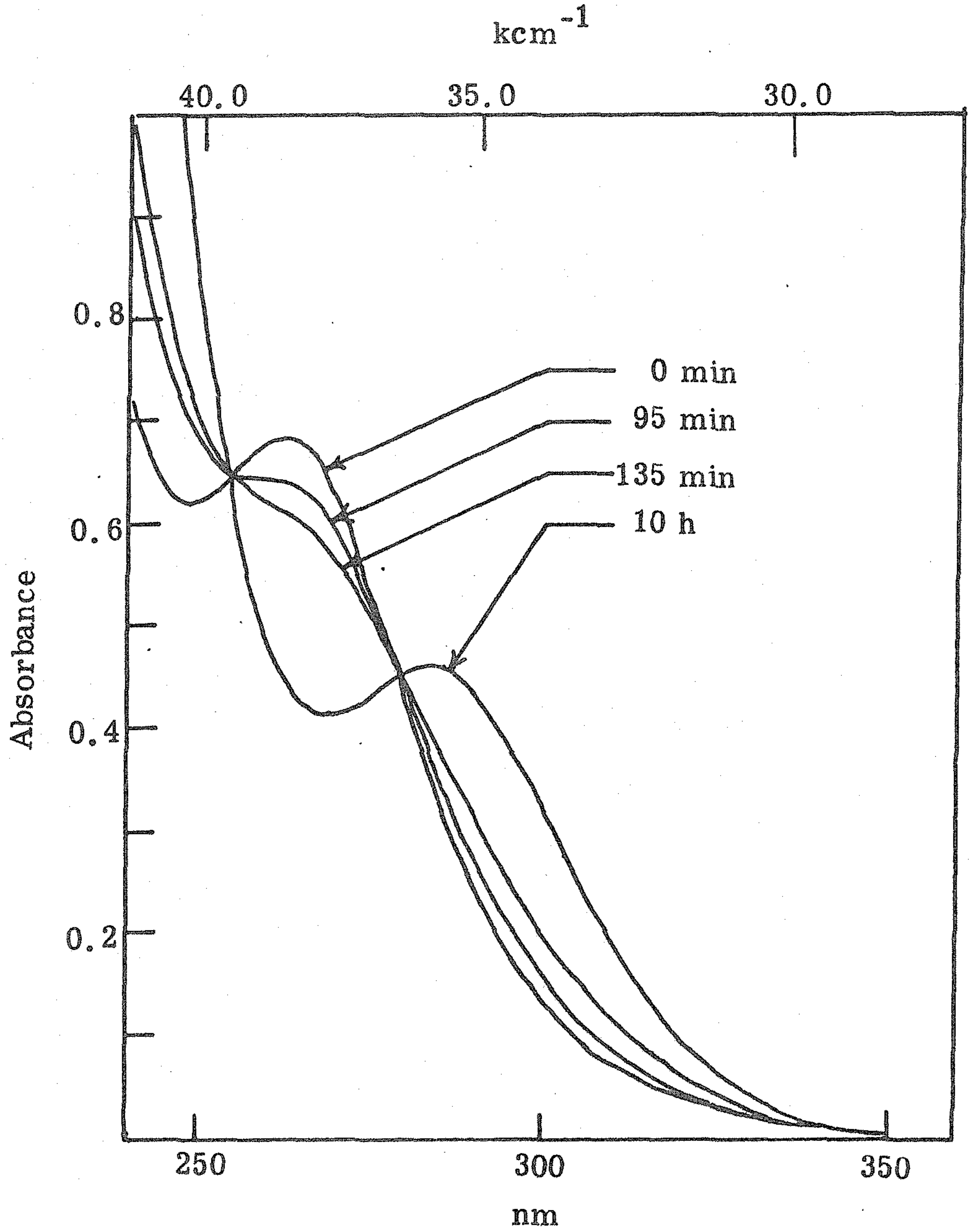


Figure I-6. Spectral changes during the reaction

$$[\mathrm{Rh(CN)_5H_2O}]^{2-} + \mathrm{Br}^- \xrightarrow{25\ ^\circ\mathrm{C}} [\mathrm{Rh(CN)_5Br}]^{3-} + \mathrm{H_2O}$$

The spectra were recorded at various intervals after the addition of KBr.

solution and in the mixed salt. Although pure samples of the potassium salts have not been obtained, it should be possible to isolate these by careful chromatographic separations, most likely by the use of high pressure liquid chromatography. It should also be possible to make a very wide variety of $[M(CN)_5X]^{n-}$ derivatives with X other than those described in this chapter (e.g., X = pyridine, amines, SO_3^{2-}, SO_4^{2-}, etc.). The availability of a large number of $[M(CN)_5X]^{n-}$ (M = Co(III), Rh(III), Ir(III)) complexes should stimulate comparisons of various spectral, reactivity, and photochemical properties of these species.

Photolysis of $[M(CN)_5X]^{n-}$ Derivatives. As is the case with many $[Co(CN)_5X]^{n-}$ complexes, as evidenced by electronic absorption spectral data summarized in Table I-2, irradiation of the $[M(CN)_5X]^{n-}$ derivatives of Rh(III) and Ir(III) in acidic or pH 7 solution results in aquation (Eq. 15):

$$[M(CN)_5X]^{n-} \xrightarrow[H_2O]{h\nu} [M(CN)_5H_2O]^{2-} + X \qquad (15)$$

Conversion to the aquo complex can be made to go to completion by continued irradiation, but removal of the solution from the irradiation source results in a very slow regeneration of the $[M(CN)_5X]^{n-}$ complex by a back anation reaction. The photoaquation reaction appears to go to completion even in the presence of a large excess of ligand X, but of course the rate of back reaction increases with increasing X concentration. One can follow the spectral changes that occur during the photolysis and can thereby confirm that aquation is complete.

Table I-2. Isosbestic Points for the Conversion

$$[M(CN)_5X]^{n-} \xrightarrow[\substack{H_2O\\pH=6}]{h\nu} [M(CN)_5(H_2O)]^{2-} + X$$

$[M(CN)_5X]^{n-}$	Isosbestic Point nm
$[Rh(CN)_5NCCH_3]^{2-}$	222, 252
$[Rh(CN)_5SCN]^{3-}$	a
$[Rh(CN)_5Cl]^{3-}$	240, 277
$[Rh(CN)_5Br]^{3-}$	255, 280
$[Rh(CN)_5I]^{3-}$	a
$[Ir(CN)_5NCCH_3]^{2-}$	223
$[Ir(CN)_5SCN]^{3-}$	257, 272
$[Ir(CN)_5Cl]^{3-}$	217, 250, 260
$[Ir(CN)_5Br]^{3-}$	226, 250
$[Ir(CN)_5I]^{3-}$	a

[a] Spectra of $[M(CN)_5X]^{n-}$ and $[M(CN)_5(H_2O)]^{2-}$ do not cross at any wavelengths under investigation.

Figure I-7 shows the spectral changes that take place during the photoaquation of $[Rh(CN)_5Br]^{3-}$, and absorption spectral data for aquation of other $[M(CN)_5X]^{n-}$ complexes is summarized in Table I-2.

Irradiation of $[Rh(CN)_5OH]^{3-}$ in pH 12 solution results in the spectral changes shown in Figure I-8. As the photolysis proceeds, the 38.4 kcm^{-1} band of $[Rh(CN)_5OH]^{3-}$ decreases in intensity, and a new band grows in at 31.2 kcm^{-1}. This is reminiscent of the spectral changes that occur during the photolysis of $[Rh(CN)_6]^{3-}$ in pH 12 solution (Figure I-5). Although the lack of a good isosbestic point around 40.0 kcm^{-1} is disappointing, it is encouraging that the 6h spectrum does not change with prolonged irradiation. This is indicative of formation of a photostable product. As is the case with $[Co(CN)_5OH]^{3-}$,[15] it is likely that the primary photoproduct is $[Rh(CN)_4(OH)_2]^{3-}$. Since the energy separation, 7200 cm^{-1}, between the 31.2 kcm^{-1} band of $[Rh(CN)_4(OH)_2]_2^{3-}$ and the 38.4 kcm^{-1} band of $[Rh(CN)_5OH]^{3-}$ is nearly the same as the 6000 cm^{-1} separation between the 44.4 kcm^{-1} band of $[Rh(CN)_6]^{3-}$ and the 38.4 kcm^{-1} band of $[Rh(CN)_5OH]^{3-}$, it is probable that trans rather than cis product is formed.[30, 31] If the solution of $[Rh(CN)_4(OH)_2]^{3-}$ is made acidic with $HClO_4$, the absorption features shift to slightly lower energy (Figure I-9), suggesting formation of $[Rh(CN)_4(H_2O)_2]^{-}$. Addition of an excess of KI to this acidic solution followed by overnight storage results in a color change from colorless to yellow. Concentration of the solution and addition to acetone gives a yellow solid which is most likely $[Rh(CN)_4I_2]^{3-}$. The absorption spectrum of this yellow solid is shown

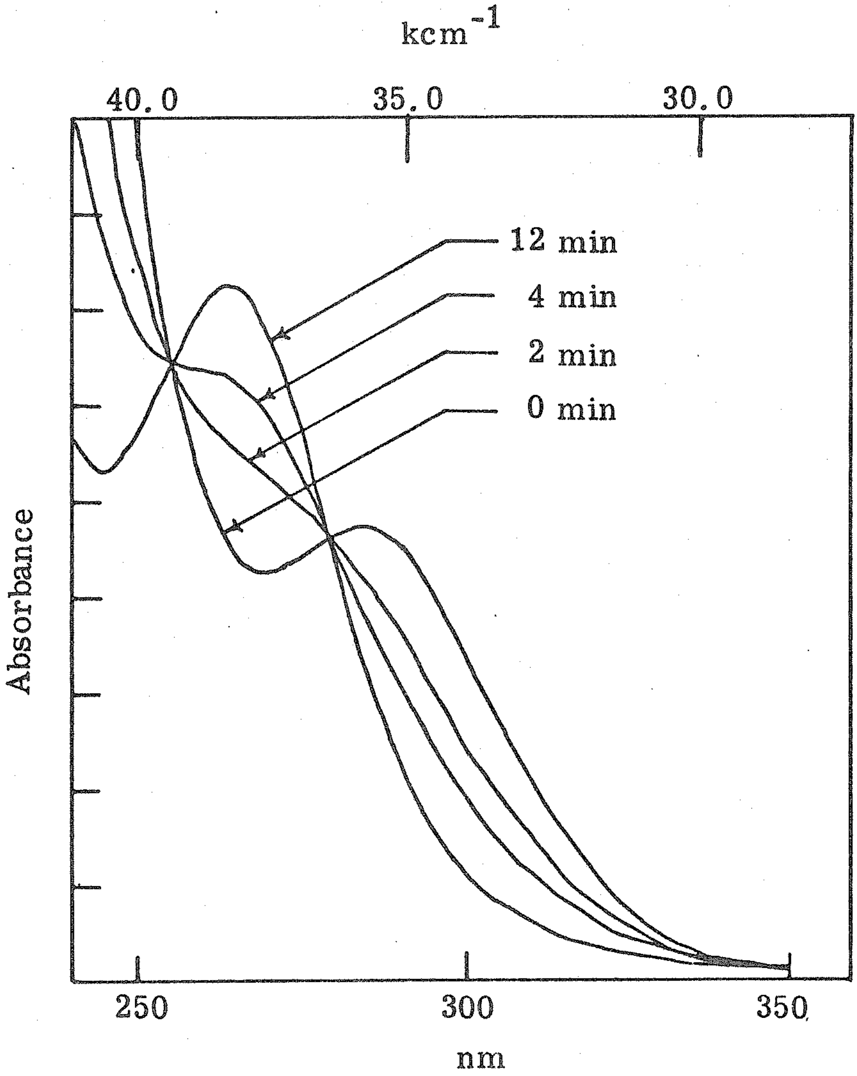


Figure I-7. Spectral changes during 254 nm irradiation of $K_3[Rh(CN)_5Br]$ in pH 6 aqueous buffer solution.

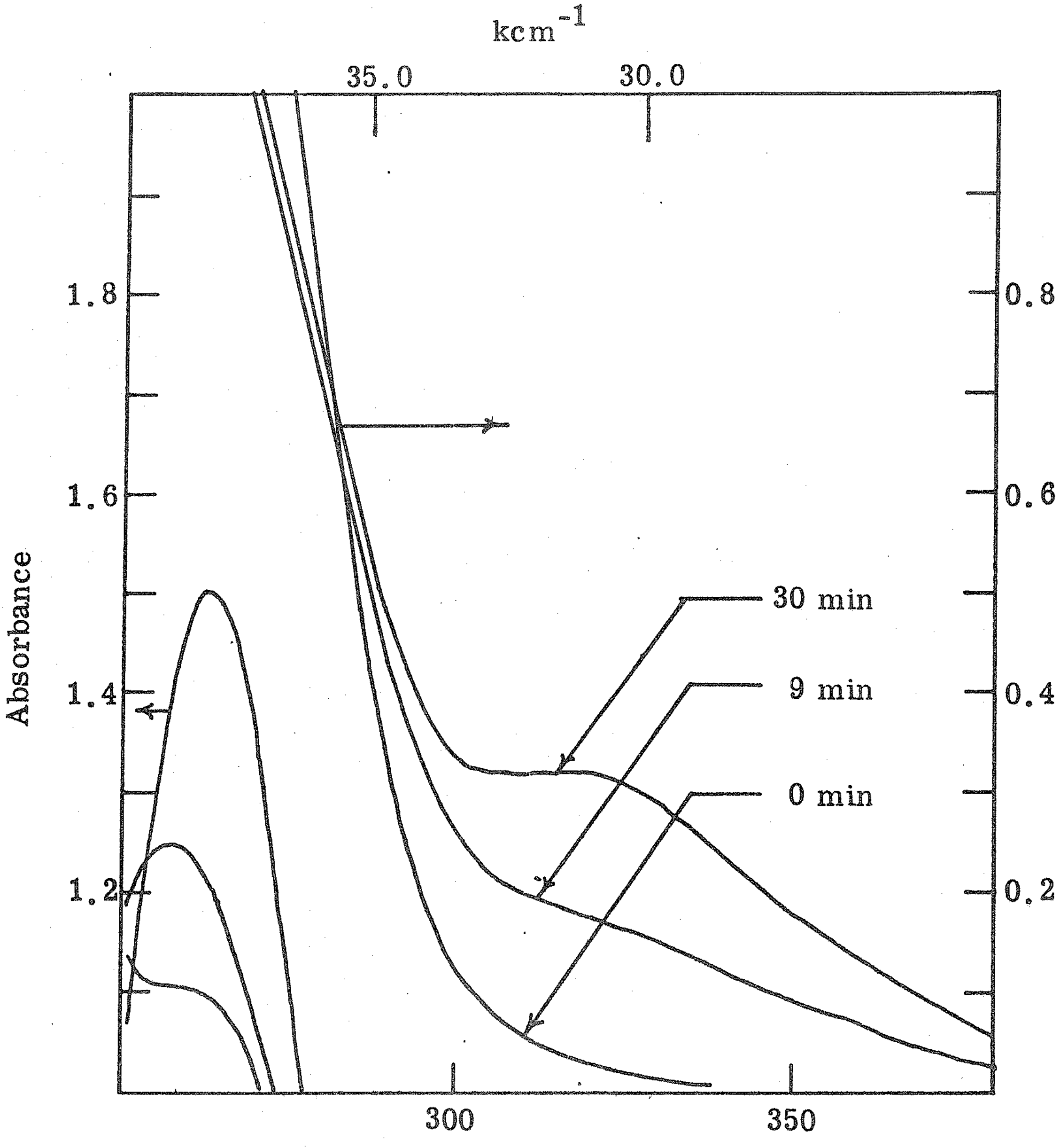


Figure I-8. Spectral changes during 254 nm irradiation of $[Rh(CN)_5OH]^{3-}$ in pH 12 solution.

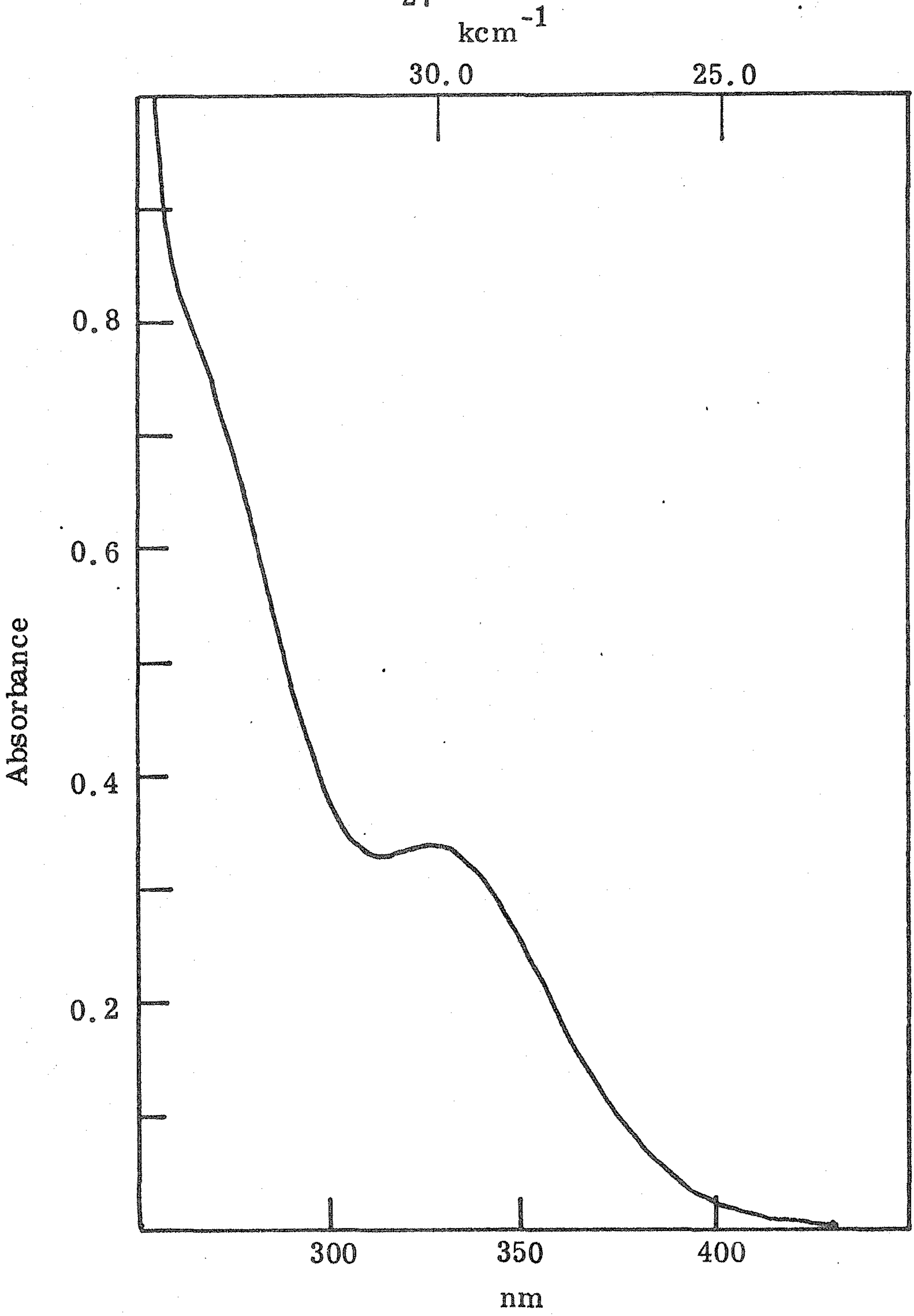


Figure I-9. Absorption spectrum of $[Rh(CN)_4(OH_2)_2]^{1-}$ in acidic solution.

in Figure I-10. Although these reactions were not further investigated, it is likely that a good synthetic route to $[M(CN)_4X_2]^{n-}$ derivatives can be developed via the following reactions (Eq. 16-18):

$$[M(CN)_5OH]^{3-} \xrightarrow[OH^-]{h\nu} [M(CN)_4(OH)_2]^{3-} + CN^- \qquad (16)$$

$$[M(CN)_4(OH)_2]^{3-} + H^+ \longrightarrow [M(CN)_4(H_2O)_2]^- \qquad (17)$$

$$[M(CN)_4(H_2O)_2]^- + X \longrightarrow [M(CN)_4X_2]^{n-} + H_2O \qquad (18)$$

Attempts were made to determine the quantum yield of aquation for $K_3[Rh(CN)_5Br]$ and $K_3[Rh(CN)_5SCN]$ and values of 0.49 and greater than one, respectively, were obtained. Little confidence should be placed in these results, as it is very likely that the potassium salts used were grossly impure. An accurate determination of the quantum yield of aquation for all the $[M(CN)_6]^{3-}$ and $[M(CN)_5X]^{n-}$ complexes should be made but must await development of a technique for isolation of pure salts.

Infrared Spectral Studies. The important features of the infrared spectra of the $K_3[M(CN)_6]$ and $K_n[M(CN)_5X]$ complexes are given in Table I-3. The ir spectra of $K_3[Rh(CN)_6]$ and $K_3[Ir(CN)_6]$ are in excellent agreement with published data,[32] and the spectra of the $[M(CN)_5X]^{n-}$ (M = Rh(III), Ir(III)) complexes are qualitatively very similar to those observed for analogous $[Co(CN)_5X]^{n-}$ complexes.[33] In addition, the position of the ir peaks attributable to the complex anions in the analyzed samples of $[Co(NH_3)_6][M(CN)_5X]$ accord well with values given in Table I-3 for the corresponding potassium salts.

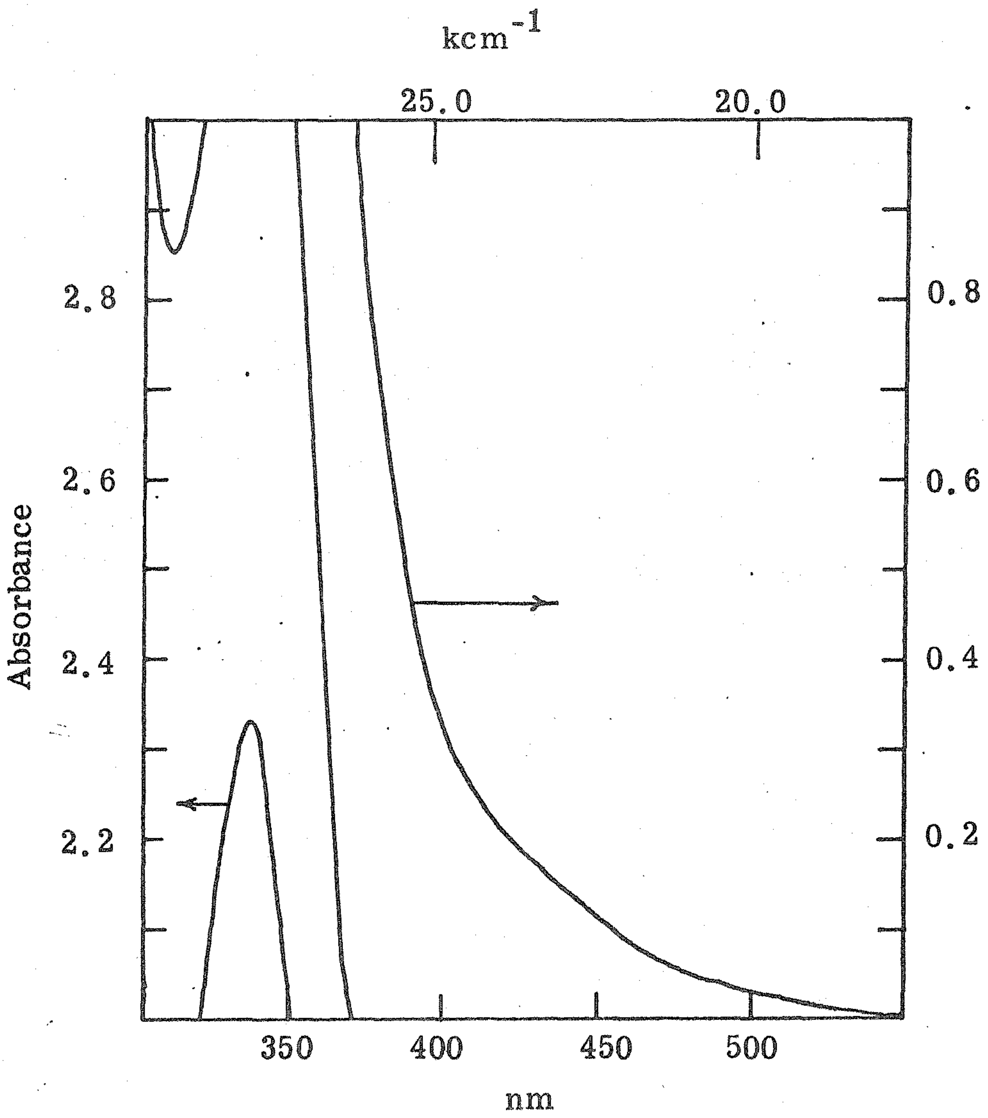


Figure I-10. Electronic spectrum of [$Rh(CN)_4I_2$]$^{3-}$ in aqueous solution.

Table I-3. Infrared Spectra of $K_n[M(CN)_5X]$ in KBr Pellets in the Range 200 - 3000 cm^{-1}

Compound	Absorptions of $M(CN)_5^{2-}$			Absorption of X	Other Peaks
	$\nu_{C\equiv N}$	δ_{MCN}	ν_{M-C}		
$K_3[Rh(CN)_6]$	2133(s)	524(m)	386(s)	------	2110(w)
		513(m)			2095(w)
$K_3[Rh(CN)_5Cl]$	2157(w)	522(w)	386(s)	------	2091(w)
	2130(s)	510(m)	366(m)		
			352(m)		
$K_3[Rh(CN)_5Br]$	2155(w)	523(w)	438(m)	------	2090(w)
	2128(s)	519(m)	386(s)		
		510(w)	360(m)		
			350(m)		
$K_3[Rh(CN)_5I]$	2156(m)	519(m)	426(m)	------	2088(w)
	2128(s)	500(m)	389(s)		
			349(m)		
$K_3[Rh(CN)_5SCN]$	2158(m)	518(m)	437(m)	2110(s)[a]	2084(w)
	2143(w, sh)	508(m, sh)	381(s)	717(w)[b]	
	2131(s)	503(m)	352(s)		
	2124(s)				
$K_2[Rh(CN)_5NCCH_3]$	2172(m)	521(m)	467(m)	2935(m)[c]	------
	2185(m)	514(m)	382(s)	2346(w)[d]	
	2138(s)		347(w)	2325(m)[d]	
				2300(m)[d]	

Table I-3 (Continued)

Compound	Absorptions of $M(CN)_5^{2-}$			Absorption of X	Other Peaks
	$\nu_{C\equiv N}$	δ_{MCN}	ν_{M-C}		
$K_3[Ir(CN)_6]$	2131(s)	525(m)	398(s)		2108(w)
		511(m)			2093(w)
$K_3[Ir(CN)_5Cl]$	2160(w)	519(m)	472(w)		
	2127(s)	508(w)	397(s)		
			372(w)		
$K_3[Ir(CN)_5Br]$	2159(m)	525(m)	470(w)		485(w)
	2130(w, sh)	516(m)	398(m)		
	2125(s)		370(w)		
$K_3[Ir(CN)_5I]$	2160(w)	522(m, sh)	402(m)		482(w)
	2132(s)	517(m)	372(w)		
	2126(s)				
$K_3[Ir(CN)_5SCN]$	2157(w)	522(w)	444(m)		
	2130(s)	510(w)	386(s)		
			366(m)		
			352(m)		
$K_2[Ir(CN)_5NCCH_3]$	2168(m)	524(m)	470(m)	2935(m)[c]	
	2129(s)	515(m)	398(s)	2331(m)[d]	

[a] Assignment uncertain.

[b] ν_{C-S}.

[c] ν_{C-H}.

[d] $\nu_{C\equiv N}$.

The assignments given in Table I-3 for the $M(CN)_5^{2-}$ modes follow closely the standard interpretation.[34] A band of medium or low intensity around 2155 cm^{-1} and an intense band at about 2130 cm^{-1} are attributable to cyano stretching, $\nu_{C\equiv N}$; the 2130 cm^{-1} band probably represents the e mode in C_{4v} symmetry. Two or three medium intensity bands, often with prominent shoulders, are observed between 500 - 550 cm^{-1}. These bands are assigned to the δ_{MCN} modes. From two to four bands are observed in the 325-475 cm^{-1} region and this group is assigned to the ν_{M-C} modes.

In addition to the $M(CN)_5^{2-}$ bands, $K_3[Rh(CN)_5SCN]$ shows a sharp, weak band at 717 cm^{-1} which is assigned to the carbon-sulfur stretch, ν_{C-S} of coordinated SCN^-. The position of this band indicates that the thiocyanate ligand is S-bonded.[35] For comparison, the ν_{C-S} band is at 718 cm^{-1} for the S-bonded $[Co(CN)_5SCN]^{3-}$ complex.[36] A peak due to ν_{C-S} in the ir spectrum of $K_3[Ir(CN)_5SCN]$ has not been identified, but the electronic spectrum of the complex suggests an S-bonded configuration (vide-infra).

The $[M(CN)_5NCCH_3]^{2-}$ complexes exhibit a sharp ν_{C-H} band at 2935 cm^{-1} and a group of bands near 2325 cm^{-1} which may be assigned to $\nu_{C\equiv N}$ of the coordinated acetonitrile. The bands at 2325 and 2300 cm^{-1} in $[Rh(CN)_5NCCH_3]^{2-}$ may be compared with the ones at 2323 and 2300 cm^{-1} in $[Rh(NH_3)_5NCCH_3][ClO_4]_3$.[37]

Electronic Spectral Studies. Electronic spectral data for the various cyanometalates in aqueous solution are set out in Table I-4.[38] Data for $[Co(CN)_6]^{3-}$ [39] and several $[Co(CN)_5X]^{n-}$ [12, 26, 33, 36] complexes

Table I-4. Electronic Absorption Spectra of $[M(CN)_5X]^{n-}$ Complexes

Compound	λ_{max} (nm)	$\bar{\nu}_{max}$ (kcm^{-1})	ϵ_{max}	Assignment	Ref.
$K_3[Co(CN)_6]$	312	32.1	243	$^1A_{1g} \rightarrow {}^1T_{1g}$	a
	260	38.5	180	$^1A_{1g} \rightarrow {}^1T_{2g}$	
	198	50.5	35,400	MLCT	
$K_3[Co(CN)_5OH]$	370	27.0	230	$^1A_1 \rightarrow {}^1E^a$	b
$K_2[Co(CN)_5H_2O]$	380	26.3	250	$^1A_1 \rightarrow {}^1E^a$	b, c
$K_3[Co(CN)_5Cl]$	391	25.6	196	$^1A_1 \rightarrow {}^1E^a$	b, d
	320sh	31.3sh	100	$^1A_1 \rightarrow {}^1A_2$	
$K_3[Co(CN)_5Br]$	396	25.3	190	$^1A_1 \rightarrow {}^1E^a$	b, d
	295sh	33.9sh	830	π LMCT	
	242	41.3	13,300	σ LMCT	
$K_3[Co(CN)_5SCN]$	378	26.5	191	$^1A_1 \rightarrow {}^1E^a$	e
	265	37.7	17,100	LMCT ($\rightarrow d_{z^2}$)	
	227	44.1	4,300	LMCT ($\rightarrow d_{x^2-y^2}$)	
	200	50.0	16,700	MLCT	

Table I-4 (Continued)

Compound	λ_{max} (nm)	$\bar{\nu}_{max}$ (kcm^{-1})	ϵ_{max}	Assignment	Ref
$K_3[Rh(CN)_6]$	260	38.5	170	$^1A_{1g} \rightarrow (^3T_{1g}, {}^3T_{2g})$?	b, g
	225sh	44.4	555	$^1A_{1g} \rightarrow {}^1T_{1g}$	
$K_2[Rh(CN)_5NCCH_3]$	245	40.8	550	$^1A_1 \rightarrow {}^1E^a$	g
$[Rh(CN)_5OH]^{3-}$	258	38.8	500	$^1A_1 \rightarrow {}^1E^a$	g
$[Rh(CN)_5H_2O]^{2-}$	265	37.7	605	$^1A_1 \rightarrow {}^1E^a$	g
$K_3[Rh(CN)_5Cl]$	277	36.1	425	$^1A_1 \rightarrow {}^1E^a$	g
$K_3[Rh(CN)_5Br]$	287(280)^h	34.8(35.7)^h	402(257)^h	$^1A_1 \rightarrow {}^1E^a$	g
	237sh	42.2sh	1,700	π LMCT	
	205	48.8	24,000	σ LMCT	
$K_3[Rh(CN)_5I]$	383(308)^h	31.9(32.5)^h	1,500(1,390)^h	$^1A_1 \rightarrow {}^1E^a$	g
	258	38.8	4,200	π LMCT	
	220	45.5	42,000	σ LMCT	
$K_3[Rh(CN)_5SCN]$	305	32.8	170	Intraligand	g
	267sh	3.75sh	940	$^1A_1 \rightarrow {}^1E^a$	
	225	44.4	18,000	LMCT ($\rightarrow d_{z^2}$)	

Table I-4. (Continued)

Compound	λ_{max} (nm)	$\bar{\nu}_{max}$ (kcm^{-1})	ϵ_{max}	Assignment	Ref
	202sh	49.5sh	9,800	LMCT ($\rightarrow d_{x^2-y^2}$)	
$K_3[Ir(CN)_6]$	i	----	---	---	g
$K_2[Ir(CN)_5NCCH_3]$	240sh	41.7sh	250	${}^1A_1 \rightarrow {}^3E^a$	g
	215sh	46.5sh	720	${}^1A_1 \rightarrow {}^1E^a$	
$[Ir(CN)_5OH]^{3-}$	260sh	38.5sh	180	${}^1A_1 \rightarrow {}^3E^a$	g
	230sh	43.5sh	630	${}^1A_1 \rightarrow {}^1E^a$	
$[Ir(CN)_5H_2O]^{2-}$	270sh	37.0sh	180	${}^1A_1 \rightarrow {}^3E^a$	g
	235	42.6	790	${}^1A_1 \rightarrow {}^1E^a$	
$K_3[Ir(CN)_5Cl]$	280sh	35.7sh	95	${}^1A_1 \rightarrow {}^3E^a$	g
	245	40.8	370	${}^1A_1 \rightarrow {}^1E^a$	
$K_3[Ir(CN)_5Br]$	290sh(285sh)^h	34.5sh(35.1sh)^h	70(55)^h	${}^1A_1 \rightarrow {}^3E^a$	g
	257(255)^h	38.9(39.2)^h	412(330)^h	${}^1A_1 \rightarrow {}^1E^a$	
	215sh	46.5sh	2,000	π LMCT	
$K_3[Ir(CN)_5I]$	320sh(310sh)^h	31.3sh(32.3sh)^h	60(75)^h	${}^1A_1 \rightarrow {}^3E^a$	g
	275(272)^h	36.4(36.8)^h	1,400(1,430)^h	${}^1A_1 \rightarrow {}^1E^a$	

Table I-4 (Continued)

Compound	λ_{max} (nm)	$\bar{\nu}_{max}$ (kcal^{-1})	ϵ_{max}	Assignment	Ref.
	230sh	43.5sh	3,000	π LMCT	
	195sh	51.3sh	21,800	σ LMCT	
$K_3[Ir(CN)_5SCN]$	285	35.1	130	Intraligand	g
	195	51.3	17,500	LMCT ($\rightarrow d_{z^2}$)	

[a] Ref. 39. [b] Ref. 33. [c] Ref. 26. [d] Ref. 12. [e] Ref. 36. [f] Ref. 40.

[g] This work. Measurements were performed at room temperature in pH 6 buffer.

[h] 77°K Measurements.

[i] No bands observed with $\bar{\nu}_{max} < 52.0$ kcm^{-1}.

are given for comparison with the analogous rhodium and iridium species. The assignments given for the low energy absorption bands are based on the LF energy level diagram shown in Figure I-11. Because of the interference of charge transfer absorption, only the LF bands in the C_{4v} complexes derived from the ${}^1A_{1g} \rightarrow {}^3T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{1g}$ octahedral transitions shall be considered in this discussion. For all the $[M(CN)_5X]^{n-}$ complexes under consideration, X has weaker LF strength than CN^-. Thus the spin-triplet and spin-singlet E^a $(e^3b_2^2a_1)$ levels are expected to be of substantially lower energy than their respective $A_2(e^4b_2b_1)$ states, as the $a_1(d_{z^2})$ orbital should be stabilized relative to $b_1(d_{x^2-y^2})$. However, before taking up the C_{4v} cases, the LF spectra of $[Rh(CN)_6]^{3-}$ and $[Ir(CN)_6]^{3-}$ will be briefly discussed.

Interpretation of the spectrum of $[Rh(CN)_6]^{3-}$ has proved to be troublesome.[39-42] Schmidtke assigned the band at 44.4 kcm^{-1} as the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition and the ill-defined shoulder at 38.5 kcm^{-1} as ${}^1A_{1g} \rightarrow ({}^3T_{1g}, {}^3T_{2g})$.[40] The spectral bands in the C_{4v} complexes (Table I-4) suggest that 44.4 kcm^{-1} is quite a reasonable position for the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ band for $[Rh(CN)_6]^{3-}$, and this assignment is adopted. There is some uncertainty concerning the assignment of the 38.5 kcm^{-1} absorption, however, due to the fact that $[Rh(CN)_5H_2O]^{2-}$, which has a maximum at 37.7 kcm^{-1}, is a likely impurity. The relative band intensity at 38.5 kcm^{-1} varies with the purity of $[Rh(CN)_6]^{3-}$, although a weak shoulder remains in the most highly purified sample obtained to date. On the other hand, the weak band at 30.8 kcm^{-1}

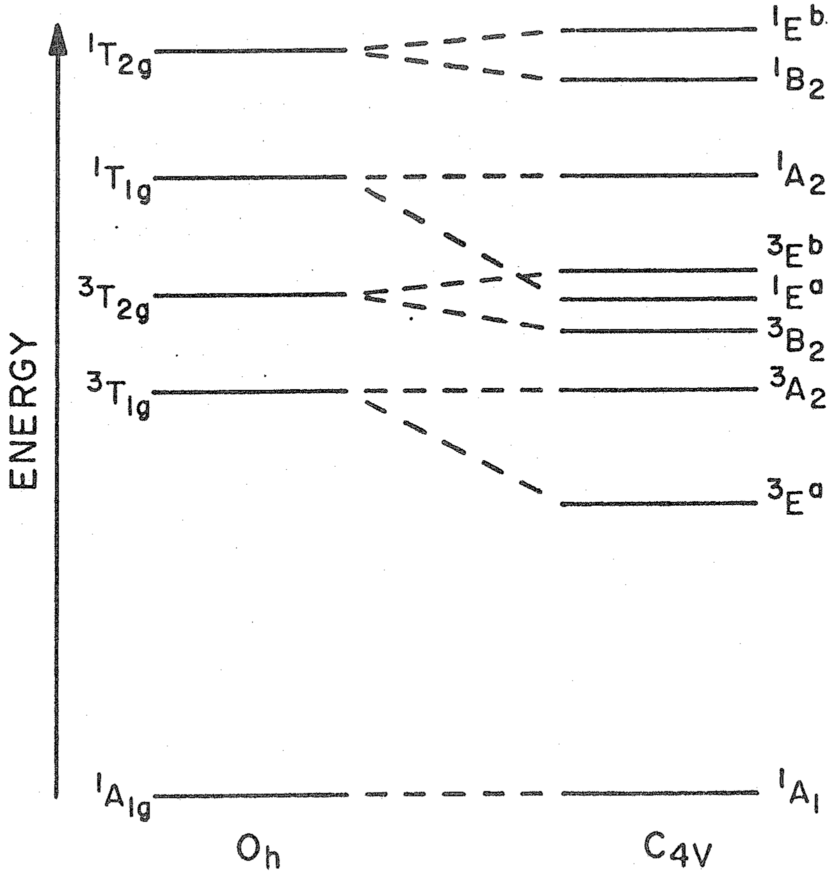


Figure I-11. Energy level diagram showing the correlation of ligand field states in O_h and C_{4V} symmetries.

reported earlier,[41] is not observed in rigorously purified samples of $[Rh(CN)_6]^{3-}$.

The third row complex $[Ir(CN)_6]^{3-}$ exhibits no band maxima at energies less than 52.0 kcm^{-1}. The assignment of the 37.0 kcm^{-1} band in $[Ir(CN)_5H_2O]^{2-}$ as $^1A_1 \rightarrow {}^3E^a$ suggests that the $^1A_{1g} \rightarrow {}^3T_{1g}$ transition in $[Ir(CN)_6]^{3-}$ occurs well above 40 kcm^{-1}, and would be overlapped by the tail of the CT absorption.

The electronic spectra of the various $[M(CN)_5X]^{n-}$ (M = Rh(III), Ir(III)) complexes are shown in Figures I-12 - I-18. The spectra of $[Rh(CN)_5Cl]^{3-}$ and $[Ir(CN)_5Cl]^{3-}$ (Figure I-12), are representative of the $[M(CN)_5X]^{n-}$ complexes and will be used for a discussion of the spectral assignments. Only one band is resolved in the spectrum of the Rh(III) complex, at 36.1 kcm^{-1} (ϵ = 425). Both the energy and the intensity of the band are consistent with its assignment as the spin-allowed $^1A_1 \rightarrow {}^1E^a$ transition. The orbitally-forbidden, equatorially-localized $^1A_1 \rightarrow {}^1A_2$ excitation would be expected to appear at approximately 44.4 kcm^{-1}, which is the position of the $^1A_{1g} \rightarrow {}^1T_{1g}$ band in $[Rh(CN)_6]^{3-}$. There is no indication in any of the $[Rh(CN)_5X]^{n-}$ spectra of the $^1A_1 \rightarrow {}^1A_2$ band, a not altogether surprising result in view of the relatively small oscillator strength anticipated for it. Careful examination of the electronic spectrum of $[Co(CN)_5Cl]^{3-}$, however, has revealed both the $^1A_1 \rightarrow {}^1E^a$ and $^1A_1 \rightarrow {}^1A_2$ bands, at 25.6 (ϵ = 196) and 31.3 (ϵ = 100) kcm^{-1}, respectively.[33] The position of the $^1A_1 \rightarrow {}^1A_2$ band in $[Co(CN)_5Cl]^{3-}$ compares favorably with the 32.1 kcm^{-1} value[39] for $^1A_{1g} \rightarrow {}^1T_{1g}$ in

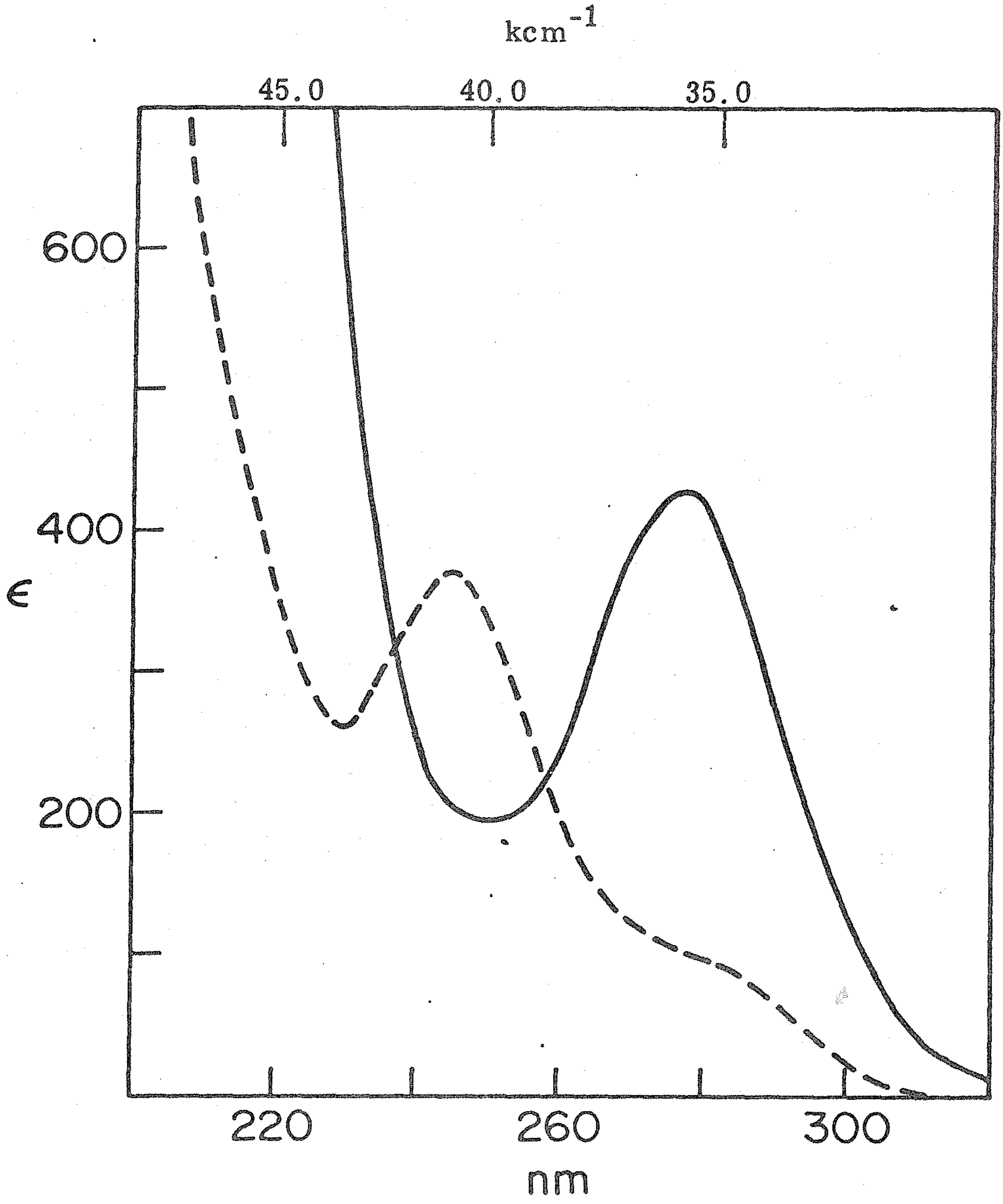


Figure I-12. Electronic spectra of $K_3[Rh(CN)_5Cl]$ (——) and $K_3[Ir(CN)_5Cl]$ (---) at pH 6 aqueous buffer solutions at 300°K.

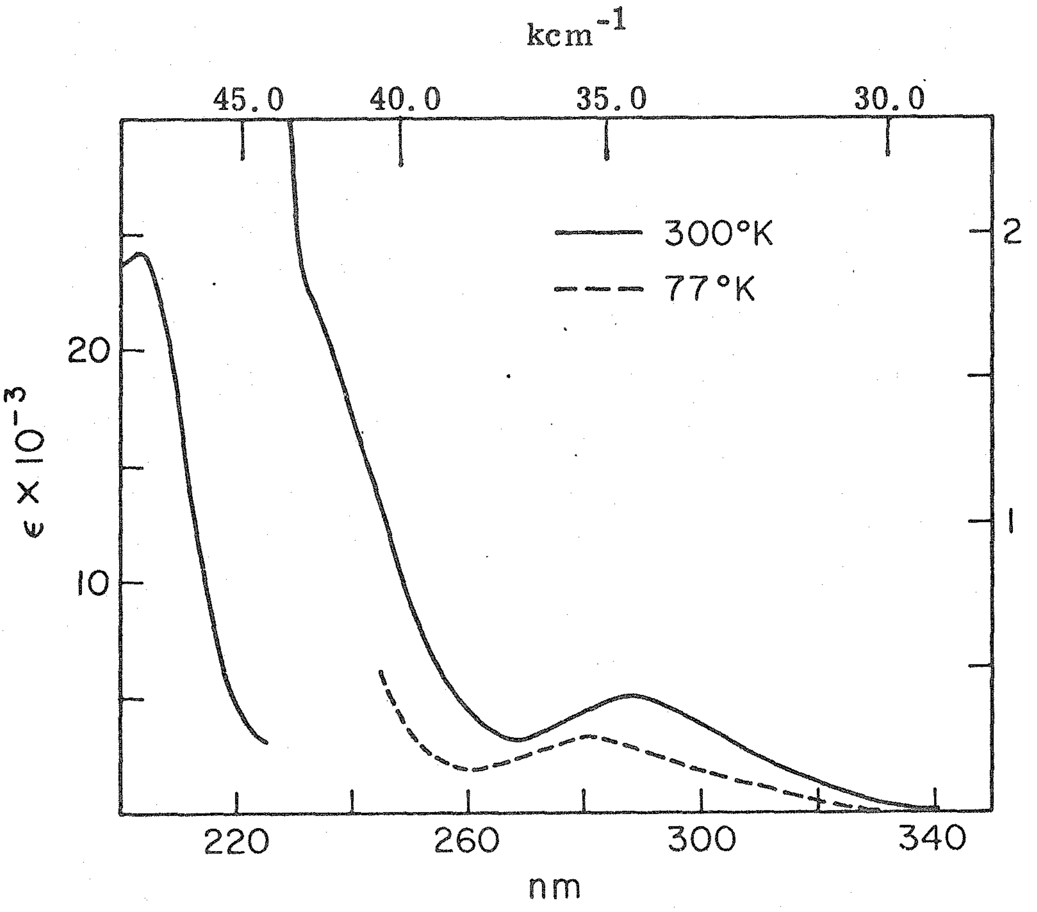


Figure I-13. Electronic spectra of $K_3[Rh(CN)_5Br]$ in pH 6 aqueous buffer solution at 300°K and in an aqueous LiCl glass at 77°K.

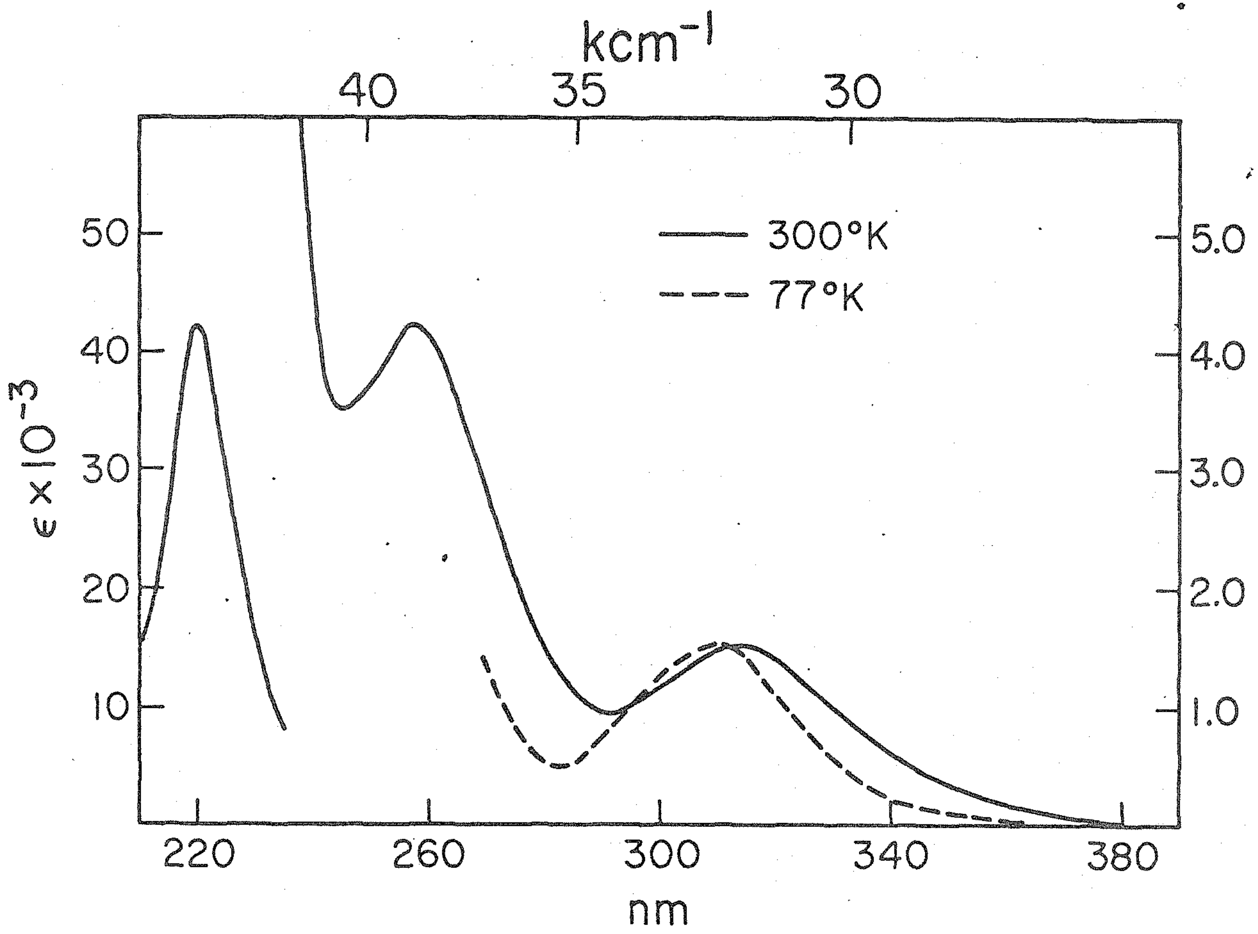


Figure I-14. Electronic spectra of $K_3[Rh(CN)_5I]$ in pH 6 aqueous buffer solution at 300°K and in an aqueous LiCl glass at 77°K.

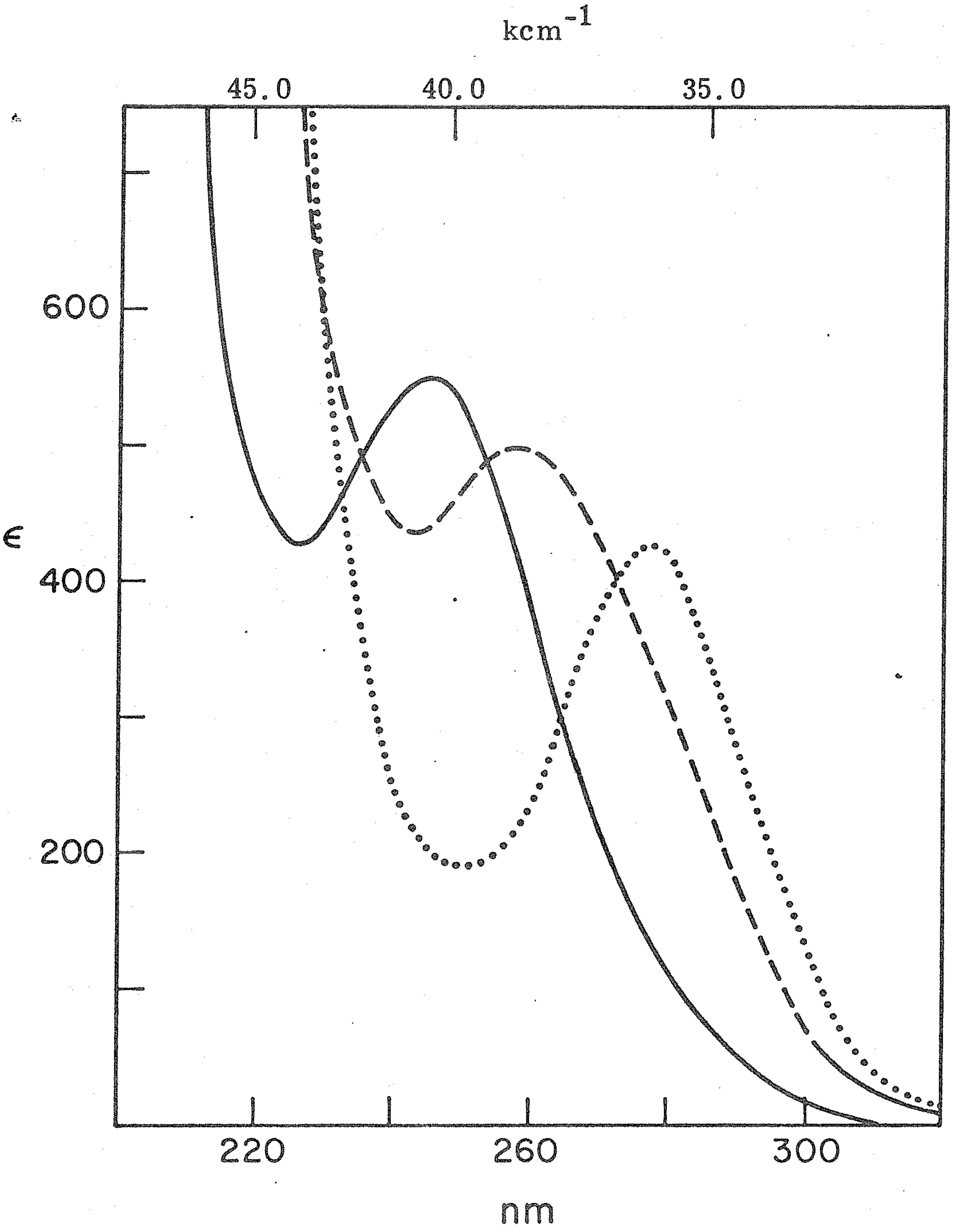


Figure I-15. Electronic spectra of $K_2[Rh(CN)_5NCCH_3]$ (——), $K_3[Rh(CN)_5OH]$ (---), and $K_3[Rh(CN)_5Cl]$ (···) in pH 6 aqueous buffer solutions at 300 °K.

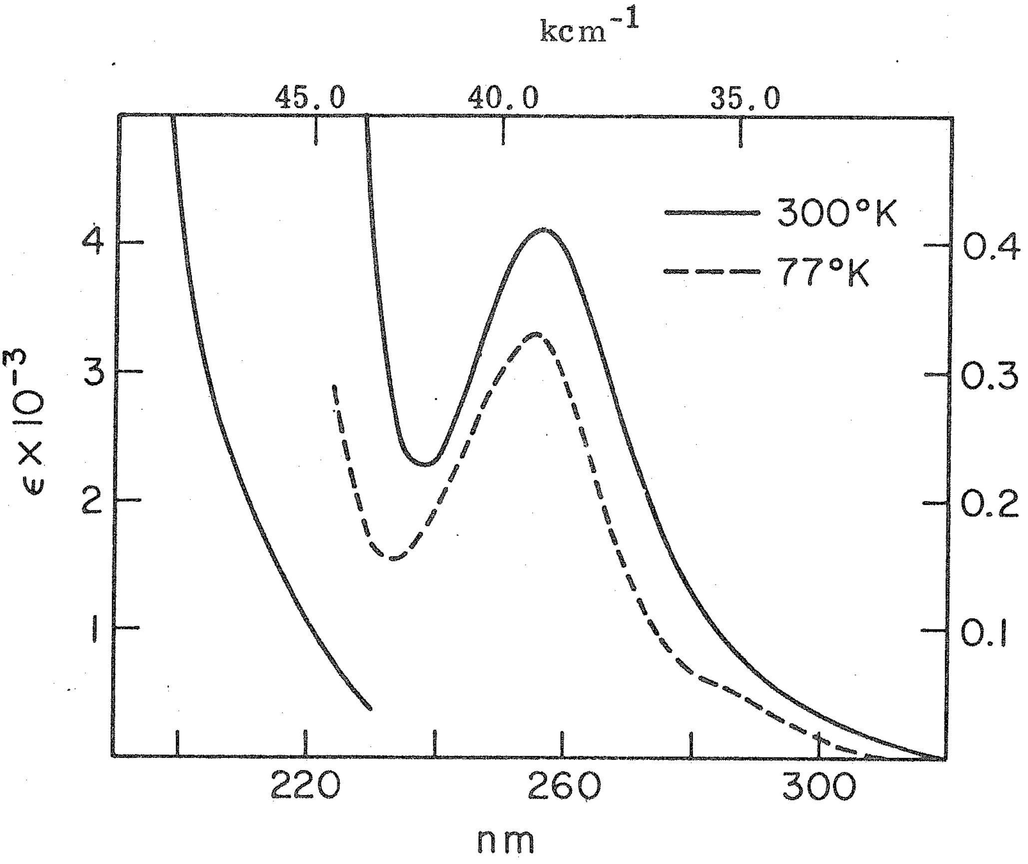


Figure I-16. Electronic spectra of $K_3[Ir(CN)_5Br]$ in pH 6 aqueous buffer solution at 300 °K and in an aqueous LiCl glass at 77°K.

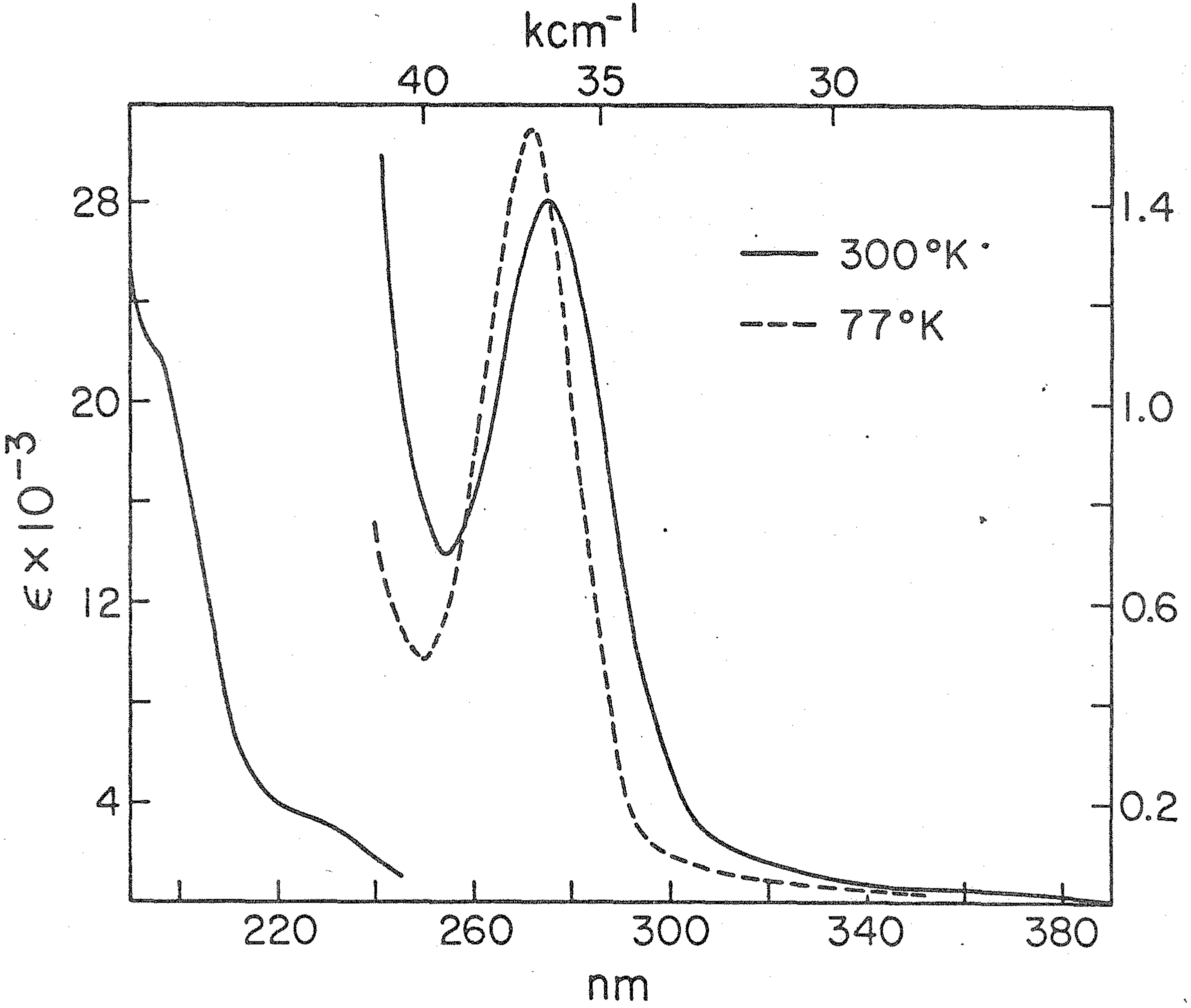


Figure I-17. Electronic spectra of $K_3[Ir(CN)_5I]$ in pH 6 aqueous buffer solution at 300°K and in an aqueous LiCl glass at 77°K.

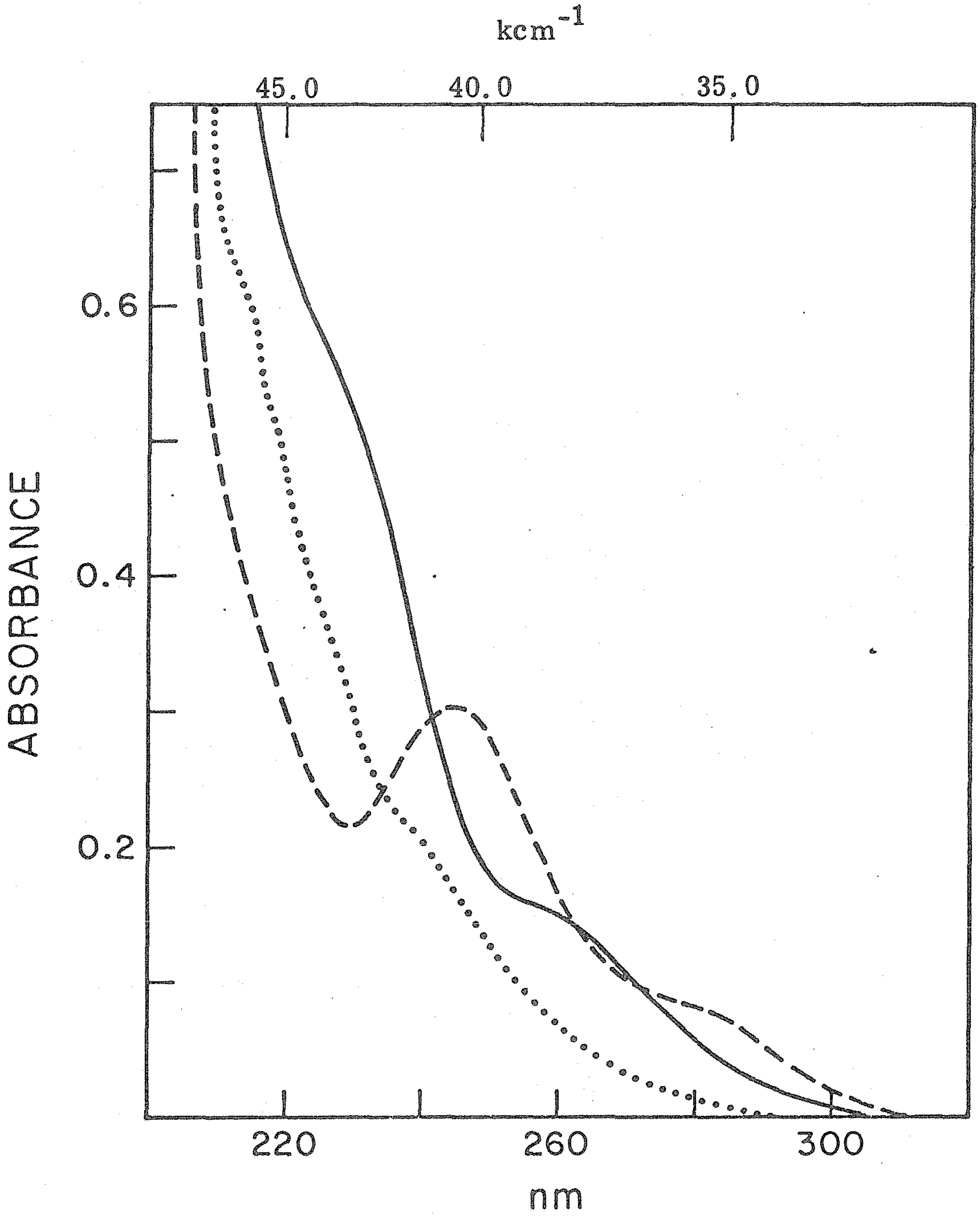


Figure I-18. Electronic spectra of $K_2[Ir(CN)_5NCCH_3]$ (——), $K_3[Ir(CN)_5OH]$ (···), and $K_3[Ir(CN)_5Cl]$ (---) in pH 6 aqueous buffer solutions at 300°K.

$[Co(CN)_6]^{3-}$, and the low intensity is also consistent with expectation. Therefore, it is probable that a $^1A_1 \rightarrow {}^1A_2$ band does in fact lie in the neighborhood of 44 kcm^{-1} in each of the $[Rh(CN)_5X]^{n-}$ complexes, but that because of CT tail absorption it is not resolved.

The spectrum of $[Ir(CN)_5Cl]^{3-}$ is similar to that of $[Rh(CN)_5Cl]^{3-}$ except that the $^1A_1 \rightarrow {}^1E^a$ band is shifted to higher energy (40.8 kcm^{-1}) and is weakly shouldered, at 35.7 kcm^{-1}. The lowest spin-forbidden LF transition, $^1A_1 \rightarrow {}^3E^a$, would be expected to be more readily observable in Ir(III) than Rh(III), because of the much larger spin-orbit coupling in the third-row central ion. The weak low energy feature in each of the $[Ir(CN)_5X]^{n-}$ complexes is therefore attributed to the $^1A_1 \rightarrow {}^3E^a$ transition.

The positions of the $^1A_1 \rightarrow {}^1E^a$ band in the $[M(CN)_5X]^{n-}$ complexes (Table I-4) are consistent with decreasing LF strength of X in the order $NCCH_3 > OH^- > H_2O > Cl^- > Br^- > I^-$ for both Rh(III) and Ir(III). A similar order has been obtained from an analysis of $[Co(CN)_5X]^{n-}$ spectra.[33]

The assignment of the observed bands in the spectra of the Rh(III) and Ir(III) complexes with X = SCN$^-$ (Figure I-19) has proved more difficult than for the other $[M(CN)_5X]^{n-}$ complexes. The spectrum of $[Co(CN)_5SCN]^{3-}$ was recently reported, and the observed bands and their assignments are as given in Table I-4, with the least energetic transition assigned as $^1A_1 \rightarrow {}^1E^a$.[36] The spectra of $[Rh(CN)_5SCN]^{3-}$ and $[Ir(CN)_5SCN]^{3-}$ are strikingly similar to that of $[Co(CN)_5SCN]^{3-}$, with a low intensity band (ϵ = 100 - 200) followed

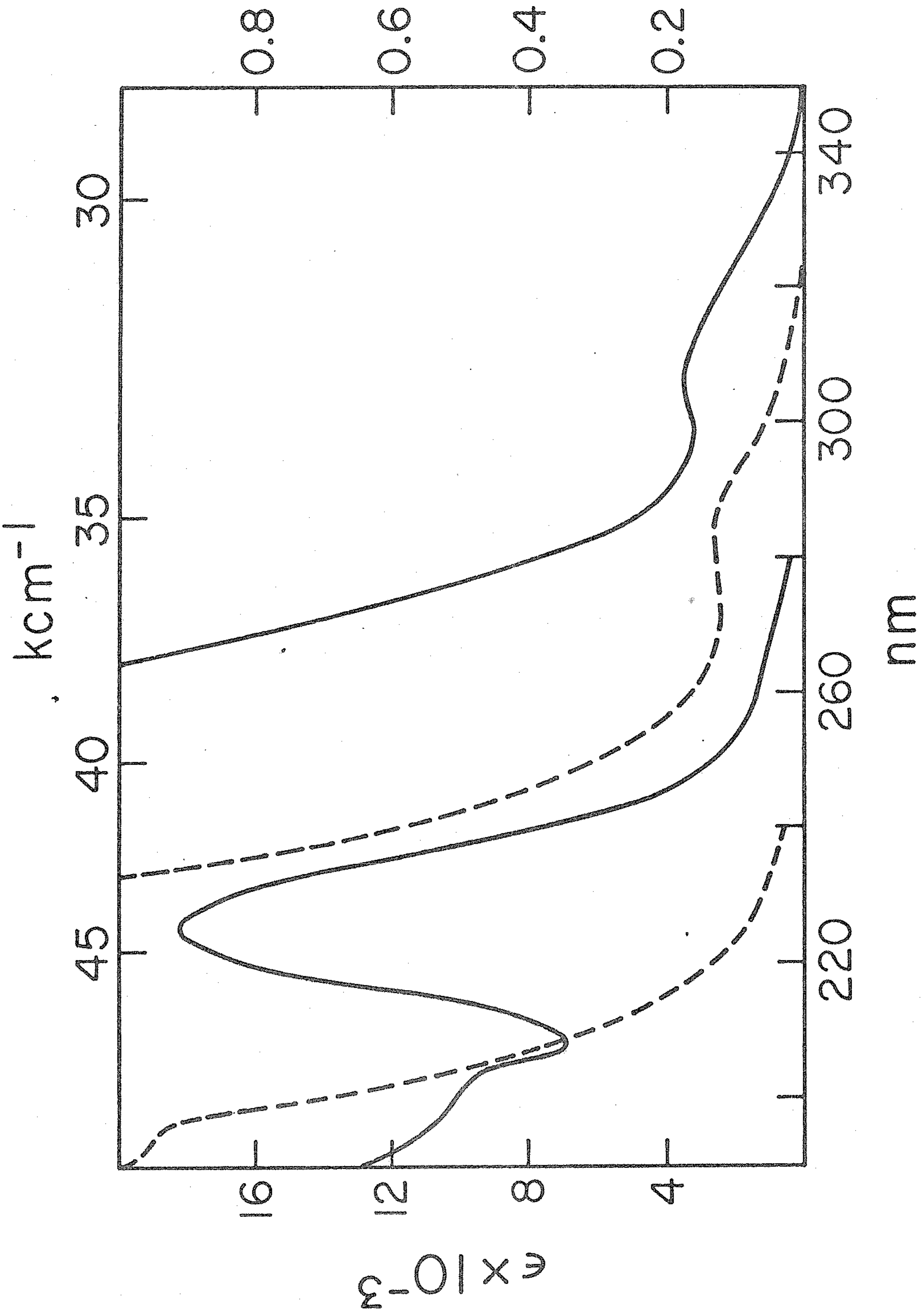


Figure I-19. Electronic spectra of $K_3[Rh(CN)_5SCN]$ (——) and $K_3[Ir(CN)_5SCN]$ (- - -) in pH 6 aqueous buffer solutions at 300°K.

by a very intense band (ϵ = 17,000 - 18,000). This similarity suggests the assignment of the first band in the Rh(III) and Ir(III) complexes as $^1A_1 \rightarrow {}^1E^a$. This interpretation is not completely satisfactory, especially for $[Ir(CN)_5SCN]^{3-}$ where the lowest band is expected to be $^1A_1 \rightarrow {}^3E^a$, as is the case with the other $[Ir(CN)_5X]^{n-}$ derivatives. Even in very concentrated solutions, a lower energy transition in $[Ir(CN)_5SCN]^{3-}$ was not found. A second possible assignment for the low energy band is thus $^1A_1 \rightarrow {}^3E^a$, and the low ϵ for the band is consistent with such an assignment. However, another problem now arises as to why the $^1A_1 \rightarrow {}^3E^a$ transition is observed in $[Rh(CN)_5SCN]^{3-}$ and not in other $[Rh(CN)_5X]^{n-}$ derivatives. Finally, a third interpretation, and the one preferred by this author, is that the band is attributable to an intraligand transition.

The electronic absorption spectra of the related complexes $[Rh(CN)_5NO_2]^{3-}$ and $[Rh(CN)_5N_3]^{3-}$ have been independently measured and are summarized in Table I-5.[29] Figure I-20 shows the spectrum of $K_3[Rh(CN)_5NO_2]$ in aqueous solution.[29] An important feature of the spectrum of each of these two complexes is the observation of a low intensity band (ϵ = 100 - 200) in the vicinity of 30.7 - 32.3 kcm^{-1}. These bands are strikingly similar to the low intensity bands at 32.8 kcm^{-1} in $K_3[Rh(CN)_5SCN]$ and 35.1 kcm^{-1} in $K_3[Ir(CN)_5SCN]$. It is likely that they are due to similar transitions. The electronic absorption spectra of nitroalkyls have been well studied, and they generally show a low intensity band (ϵ = 20 - 40) in the region 35.7 - 37.0 kcm^{-1}.[43] This band has been assigned as an $n \rightarrow \pi^*$ transition

Table I-5. Electronic Spectra of $K_3[Rh(CN)_5NO_2]$ and $K_3[Rh(CN)_5N_3]$ in Aqueous Solution[a]

Compound	λ_{max} (nm)	$\bar{\nu}_{max}$ (kcm^{-1})	ϵ_{max}	Assignment
$K_3[Rh(CN)_5NO_2]$	310	32.3	125	$n \rightarrow \pi^*$
	232 sh	43.1	3,336	MLCT
	203	49.3	14,089	LMCT
$K_3[Rh(CN)_5N_3]$	325	30.8	180	$\pi_y \rightarrow \pi_x^*$
	272	36.8	2,400	LMCT
	244	41.0	3,920	LMCT

[a] Ref. 29.

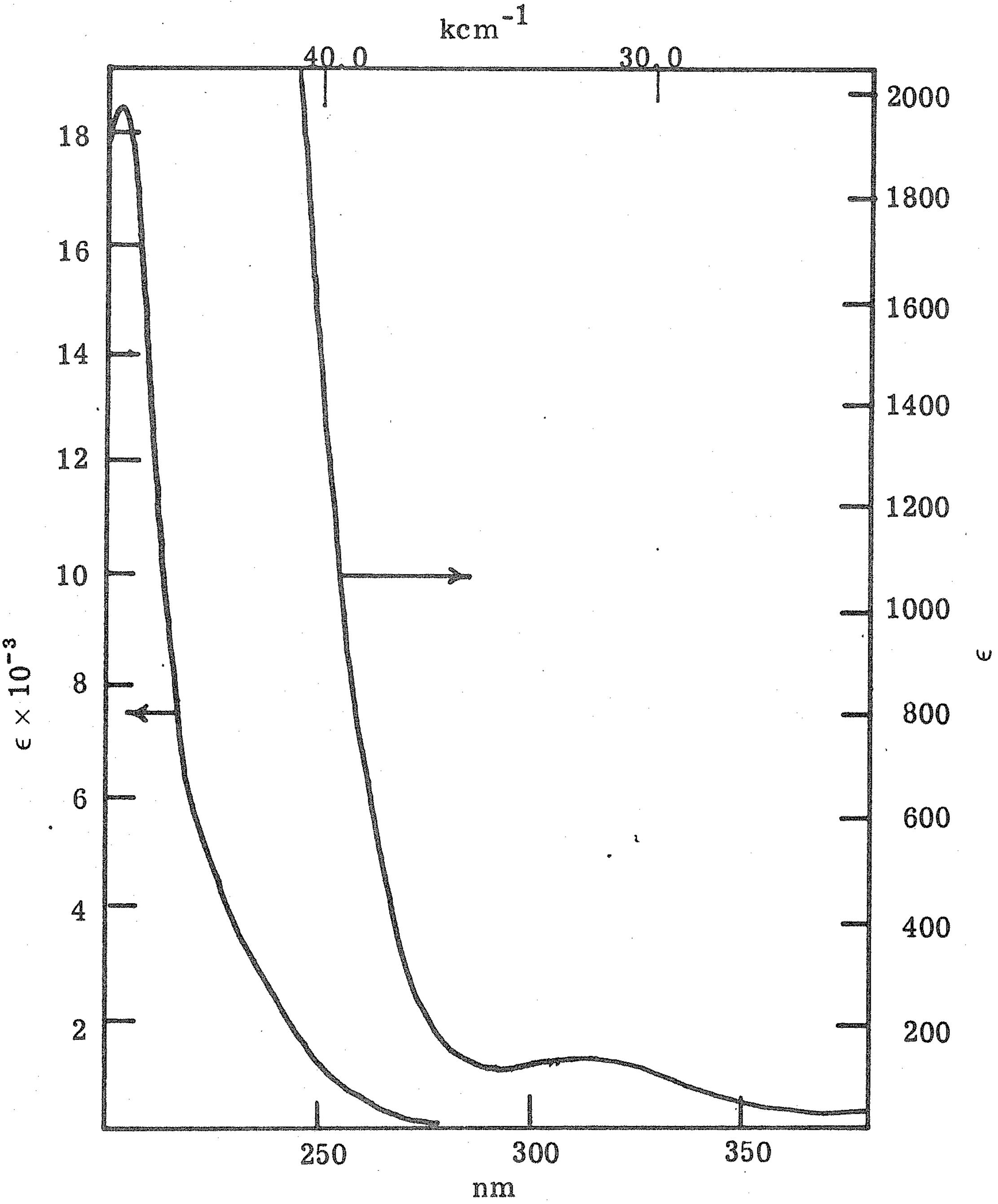


Figure I-20. Electronic spectrum of $K_3[Rh(CN)_5NO_2]$ in aqueous solution.

of the nitro group. It is thus likely that the band at 32.3 $\mathrm{kcm^{-1}}$ in $K_3[Rh(CN)_5NO_2]$ is an $n \rightarrow \pi^*$ transition of the nitro ligand, and it is assigned accordingly. This is quite a reasonable assignment since the nitro ligand lies between CN^- and H_2O in the spectrochemical series of the related $[Co(CN)_5X]^{n-}$ complexes,[33] and any LF bands are thus expected at energy much higher than 32.3 $\mathrm{kcm^{-1}}$. Electronic spectra of alkyl azides have also been extensively studied.[44] The spectra show a low intensity band ($\epsilon = 20 - 40$) in the vicinity of 34.6 - 35.5 $\mathrm{kcm^{-1}}$ that has been assigned as a $\pi_y \rightarrow \pi_x{}^*$ transition of the azido group. In a bent alkyl azide, as well as in a bent metal azide, this $\pi_y \rightarrow \pi_x{}^*$ transition is closely related to the $n \rightarrow \pi^*$ transition of organic ketones, and to the $n \rightarrow \pi^*$ transition of the nitro ligand.[44] A likely assignment for the 30.8 $\mathrm{kcm^{-1}}$ band in $K_3[Rh(CN)_5N_3]$ is thus $\pi_y \rightarrow \pi_x{}^*$ of the coordinated azide. These assignments then suggest that the low intensity bands in the spectra of the SCN^- complexes are due to an intraligand transition of the $\pi_y \rightarrow \pi_x{}^*$ type, and they are assigned accordingly. Indeed in the few reported spectra of alkyl thiocyanates, a low intensity band ($\epsilon = 10 - 50$) is observed in the region 40.0 - 40.8 $\mathrm{kcm^{-1}}$, consistent with this assignment.[45]

The ligand field bands in these complexes are obscured by charge transfer transitions. However, in the spectrum of $K_3[Rh(CN)_5SCN]$, a weak shoulder is evident at 37.5 $\mathrm{kcm^{-1}}$ ($\epsilon = 940$) which may be assigned as the ${}^1A_1 \rightarrow {}^1E^a$ LF transition. This assignment places SCN^- at about the position of H_2O in the spectrochemical series, consistent with the series found for $[Co(CN)_5X]^{n-}$ complexes.[33]

For $[M(CN)_5X]^{n-}$ complexes with X = Br^- or I^-, one or two relatively intense absorption bands are observed at higher energies than the $^1A_1 \rightarrow {}^1E^a$ transition. The spectrum of $[Rh(CN)_5I]^{3-}$, for example, shows well-resolved bands at 38.8 (ϵ = 4200) and 45.5 (ϵ = 42,000) kcm^{-1}, in addition to a $^1A_1 \rightarrow {}^1E^a$ band at 31.9 (ϵ = 1500) kcm^{-1} (Figure I-14). These additional bands are much too intense to be attributable to LF transitions, so they must represent ligand (X) → metal charge transfer (LMCT) excitation processes. There are two allowed LMCT transitions from halide valence p orbitals to a_1 (d_{z^2}), which is the lowest metal virtual orbital. These transitions are $^1A_1 \rightarrow {}^1E$ ($e\pi X \rightarrow a_1d_{z^2}$) and $^1A_1 \rightarrow {}^1A_1$ ($a_1\sigma X \rightarrow a_1d_{z^2}$), abbreviated πLMCT and σLMCT, respectively. Simple theoretical reasoning, which places the σ-bonding $a_1\sigma X$ orbital lower than the $e\pi X$ level, as well as established experimental patterns in the LMCT spectra of a variety of halometalate complexes,[46] lead to the expectation that the σLMCT band will be of higher energy and have substantially greater intensity than the πLMCT absorption. Thus the 38.8 and 45.5-kcm^{-1} bands in $[Rh(CN)_5I]^{3-}$ are assigned to πLMCT and σLMCT transitions, respectively. Analogous LMCT assignments are given in Table I-4 for the intense bands observed in $[Rh(CN)_5Br]^{3-}$, $[Ir(CN)_5Br]^{3-}$, and $[Ir(CN)_5I]^{3-}$.

The charge transfer transitions in the SCN^-, NO_2^-, and N_3^- derivatives may be assigned in accordance with the assignments given for the analogous cobalt species by Miskowski and Gray.[33] The

44.4 kcm^{-1} and 49.5 kcm^{-1} bands in $K_3[Rh(CN)_5SCN]$ are thus LMCT ($\rightarrow d_{z^2}$) and LMCT ($\rightarrow d_{x^2-y^2}$), respectively. The 51.3 kcm^{-1} band in $K_3[Ir(CN)_5SCN]$ is LMCT ($\rightarrow d_{z^2}$). The 43.1 kcm^{-1} band in $K_3[Rh(CN)_5NO_2]$ may be assigned as MLCT and the 49.3 kcm^{-1} band as LMCT. These follow the assignments of Fenske for the hexanitrometalates.[47] The intense bands in the spectrum of $K_3[Rh(CN)_5N_3]$ must also be LMCT.

Comparison of Photochemical Properties of Cyanide Complexes of Co(III), Rh(III), and Ir(III). The results presented in this chapter clearly show that the photochemical properties of the $[M(CN)_6]^{3-}$ (M = Co(III), Rh(III), Ir(III)) complexes are parallel, each giving the pentacyanoaquo complex as the only photoproduct when photolysis is conducted in acidic media, and giving the pentacyanohydroxy complex as the initial photoproduct when irradiation is carried out in basic media. Furthermore, it has been shown that irradiation of $[M(CN)_5X]^{n-}$ (M = Rh(III), Ir(III)) derivatives gives similar photochemistry to that observed for analogous $[Co(CN)_5X]^{n-}$ complexes. Now that the photochemistry has been shown to be essentially identical for the various cyanometalates, a comparison of the photochemical quantum yields would be extremely interesting. Unfortunately, impure samples and experimental problems have precluded accurate determination of the quantum yields for the Rh(III) and Ir(III) complexes, and such a comparison will have to await future experiments in this area.

References

1. E. Koerner von Gustorf and F. W. Grevels, Fortschr. Chem. Forsch., 13, 366 (1969).
2. V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, 1970.
3. M. S. Wrighton, Chem. Rev., submitted for publication.
4. G. Ferraudi and J. F. Endicott, Chem. Commun., 1973, 674.
5. T. L. Kelly and J. F. Endicott, J. Phys. Chem., 76, 1937 (1972).
6. T. L. Kelly and J. F. Endicott, Chem. Commun., 1971, 1061.
7. C. Kutal and A. W. Adamson, Inorg. Chem., 12, 1454 (1973).
8. T. L. Kelly and J. F. Endicott, J. Amer. Chem. Soc., 94, 1797 (1972).
9. T. L. Kelly and J. F. Endicott, J. Amer. Chem. Soc., 92, 5733 (1970).
10. J. L. Reed, F. Wang, and F. Basolo, J. Amer. Chem. Soc., 94, 7173 (1972).
11. G. Ferraudi and J. F. Endicott, J. Amer. Chem. Soc., 95, 2371 (1973).
12. A. W. Adamson and A. H. Sporer, J. Amer. Chem. Soc., 95, 2371 (1973).
13. A. W. Adamson and A. H. Sporer, J. Inorg. Nucl. Chem., 8, 209 (1958).
14. L. Moggi, F. Boletta, V. Balzani, and F. Scandola, J. Inorg. Nucl. Chem., 28, 2589 (1966).
15. M. Wrighton and D. Bredesen, Inorg. Chem., 12, 1707 (1973).

16. A. W. Adamson, A. Chiang, E. Zinato, *J. Amer. Chem. Soc.*, **91**, 5467 (1969).

17. M. S. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 5254 (1971).

18. M. S. Wrighton, H. B. Gray, G. S. Hammond, and V. Miskowski, *Inorg. Chem.*, **12**, 740 (1973).

19. B. M. Chadwick and A. G. Sharpe, *Advan. Inorg. Chem. Radiochem.*, **8**, 83 (1966).

20. A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962).

21. D. N. Lawson, M. J. Mays, and G. Wilkinson, *J. Chem. Soc. A*, **52**, (1966).

22. R. A. Jewsbury and J. P. Maher, *J. Chem. Soc. A*, 2847 (1971); 2089 (1972).

23. a) M. L. H. Green, *Angew. Chem.*, **72**, 719 (1960); b) L. L. Lohr, Jr., and W. N. Lipscomb, *Inorg. Chem.*, **3**, 22 (1964).

24. F. Holzl, *Mh. Chem.*, **73**, 1 (1941).

25. J. H. Bayston, R. N. Beale, N. Kelso King, and M. E. Winfield, *Australian J. Chem.*, **16**, 954 (1963).

26. A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, **83**, 509 (1961).

27. A solution containing exactly 10^{-3} moles of $K_3[Rh(CN)_6]$ was prepared and adjusted to pH = 2.95 [$H^+ = 1.12 \times 10^{-3}$]. The solution was irradiated and the uv spectrum and pH monitored. When the uv spectrum showed the reaction to be essentially complete, the pH had changed to a final value of 3.50 [H^+ =

0.32 x 10^{-3}]. This corresponds to 0.8 moles of CN^- released.

28. A. Haim and W. K. Wilmarth, Inorg. Chem., 1, 573 (1962).
29. Private communication from John Robbins.
30. R. A. D. Wentworth and T. S. Piper, Inorg. Chem., 4, 709 (1965).
31. R. Krishnamurthy, W. B. Schaap, and J. P. Perumareddi, Inorg. Chem., 6, 1338 (1967).
32. L. H. Jones, J. Chem. Phys., 41, 856 (1964).
33. V. M. Miskowski and H. B. Gray, to be submitted.
34. D. M. Adams, "Metal Ligand and Related Vibrations," St. Martin's Press, New York, 1968, Chapter 3.
35. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, 1970, p. 187.
36. D. F. Gutterman and H. B. Gray, J. Amer. Chem. Soc., 93, 3364 (1971).
37. R. D. Foust, Jr., and P. C. Ford, Inorg. Chem., 11, 899 (1972).
38. Solution spectra for the $[Co(NH_3)_6][M(CN)_5X]$ complexes were difficult to obtain, owing to the very low solubilities of these salts. However, the uv spectra of the compounds containing $[Rh(CN)_5Br]^{3-}$, $[Rh(CN)_5I]^{3-}$, and $[Ir(CN)_5I]^{3-}$ were measured. In these three cases, the positions and intensities of the uv bands attributable to the complex anions are in excellent agreement with corresponding values given in Table IV.
39. J. J. Alexander and H. B. Gray, J. Amer. Chem. Soc., 90, 4260 (1968).

40. H. H. Schmidtke, Z. Physik. Chem., Frankfurt, 40, 96 (1966).

41. J. J. Alexander and H. B. Gray, Coord. Chem. Rev., 2, 29 (1967).

42. F. Zuloaga and G. Jauregui, Rev. Latinoamer. Quim., 2, 97 (1971).

43. H. H. Jaffé and Milton Orchin, "Theory and Applications of Ultraviolet Spectroscopy, John Wiley and Sons, New York 1962.

44. W. O. Closson and H. B. Gray, J. Amer. Chem. Soc., 85, 290 (1963).

45. S. F. Mason, Quart. Revs., 15, 287 (1951).

46. W. R. Mason and H. B. Gray, J. Amer. Chem. Soc., 90, 5721 (1968).

47. K. G. Caulton and R. F. Fenske, Inorg. Chem., 6, 562 (1967).

CHAPTER II

Photochemical Reductive Elimination Reactions of Some Iridium Oxygen and Dihydride Complexes

Introduction

Oxidative-addition reactions of small molecules to square-planar complexes of iridium(I) have been extensively investigated by many workers.[1-13] Vaska's complex, $IrCl(CO)(Ph_3P)_2$, and the related complexes $IrI(CO)(Ph_3P)_2$, $[Ir(2\text{-phos})_2]^+$,[14] and $[Ir(2\text{=phos})_2]^+$,[14] among others, oxidatively add molecular oxygen, hydrogen, hydrogen chloride, and a large variety of other small molecules.[1,8] In many cases these oxidative addition reactions are reversible, and by a proper choice of experimental conditions, the original square planar compound can be regenerated from the adduct. However, of the O_2, H_2, and HCl adducts of the four complexes mentioned above, only $IrCl(CO)(Ph_3P)_2O_2$ and $IrCl(CO)(Ph_3P)_2H_2$ will undergo the reverse reductive-elimination reaction under mild conditions.[1,8,10] For example, $IrCl(CO)(Ph_3P)_2O_2$ will lose oxygen when a solution of the complex is purged with an inert gas, or when the solid is heated. By comparison, loss of oxygen will not occur from purged solutions of $[Ir(2\text{-phos})_2O_2]^+$ or when the solid is heated in vacuo at 110° for 24 h.[8]

This chapter is a report of successful reductive-elimination of molecular hydrogen and oxygen, and in one case hydrogen chloride, from the adducts of these thermally "irreversible" complexes, by uv irradiation of solutions of the complexes under an inert gas purge, illustrated by the reaction

$$[\mathrm{Ir(2\text{-}phos)_2O_2}]^+ \xrightarrow[\text{Ar purge}]{h\nu} [\mathrm{Ir(2\text{-}phos)_2}]^+ + \mathrm{O_2} \qquad (1)$$

This photochemical reductive-elimination has also been observed in low temperature glasses. To the author's knowledge this is the first report of a light induced reductive-elimination reaction, and although it has been briefly mentioned that some of these complexes are light sensitive, this is the first extensive study of the photochemical properties of these adducts. Vaska has briefly reported that the orange crystals of $IrCl(CO)(PPh_3)_2O_2$ are sensitive to light and change to green and then to blue-black on prolonged exposure, and that the photoproduct probably contains triphenylphosphine oxide and an Ir(IV) complex.[4] In another communication only this brief statement was made: "It has been observed that the deoxygenation reaction of $IrCl(CO)(PPh_3)_2O_2$ is photocatalyzed."[11]

The observed deoxygenation and dehydrogenation reactions prompted an investigation into the possibility of developing a photocatalytic oxygenation or hydrogenation system, and the results of this study are reported herein. The hope of such a study was that molecular oxygen would leave the complexes in a highly energetic or activated state, or that hydrogen atoms are produced in the photolysis, and that these species would then subsequently attack substrate molecules.

Experimental

Samples of $IrCl(CO)(Ph_3P)_2$ were purchased from Alfa Chemical Corporation and were used without further purification. $[Ir(2\text{-phos})_2]Cl$ and $[Ir(2{=}phos)_2]Cl$ were prepared by published methods,[8] and $IrI(CO)(Ph_3P)_2$ was a gift from Professor Joe Gordon and $[Co(2{=}phos)_2O_2]ClO_4$ from Dr. Vince Miskowski. Infrared and electronic absorption spectra of the complexes are in excellent agreement with published data.[1,8,9] Tetramethylethylene (TME) and 1-heptene were obtained from the Aldrich Chemical Corporation. All other chemicals used were reagent grade.

Preparation of Dioxygen Complexes. $IrCl(CO)(Ph_3P)_2O_2$ and $IrI(CO)(Ph_3P)_2O_2$ were prepared by passing oxygen gas through benzene solutions of $IrCl(CO)(Ph_3P)_2$ and $IrI(CO)(Ph_3P)_2$, respectively, until the characteristic visible absorption bands of the square planar complexes disappeared. $IrCl(CO)(Ph_3P)_2O_2$ was isolated by concentrating the solution, cooling in an ice bath under an atmosphere of oxygen, and filtering the resultant precipitate. $IrI(CO)(Ph_3P)_2O_2$ was not isolated from solution. $[Ir(2\text{-phos})_2O_2]Cl$ and $[Ir(2{=}phos)_2O_2]Cl$ were similarly prepared in ethanol or acetonitrile and were isolated as crystalline salts.

Preparation of Dihydride and Hydrogen Chloride Complexes. These complexes were prepared in a similar manner to the dioxygen complexes, except that hydrogen and hydrogen chloride gases were used. The reactions were much faster than the corresponding reactions with oxygen, and solid complexes were isolated in all cases.

Solution Irradiation Procedure. The complex to be studied was dissolved in a suitable solvent (benzene for neutral complexes; ethanol or acetonitrile for ionic complexes) and placed in a 1 cm quartz spectrophotometric cell fitted with a 3 inch neck and a septum cap. A gas purge could be affected by passing the appropriate gas through the septum cap using standard syringe needle techniques.[15] Irradiation was carried out with a 150 watt medium pressure Hg lamp equipped with filters which pass only 366 nm (27.3 kcm^{-1}) light. The quartz cell was placed in a jacketed cell holder in front of the lamp and cooled with tap water. The cell was periodically removed and the absorption spectrum of the solution measured.

Low Temperature Glass Irradiation Procedure. The appropriate complex was dissolved in a 12:1 EPA:chloroform mixture and placed in a 20 cm long-15 mm O.D. glass tube with a round bottom. The solution was then cooled with liquid nitrogen in an unsilvered pyrex dewar to yield a clear glass. Photolysis was conducted by placing the dewar in front of a Hanovia 1000 watt Hg-Xe lamp equipped with water and pyrex filters. A portion of the dewar was covered with black tape to limit the area of irradiation to about one inch of the sample tube.

Photocatalytic Study. A photolysis set-up consisting of three 6 inch tubes, each fitted with a condenser and a gas purging system, was assembed. Two tubes were half-filled with a solution of $\mathrm{IrCl(CO)(Ph_3P)_2}$ and the appropriate olefin in benzene. The third tube contained only the olefin in benzene. One tube with $\mathrm{IrCl(CO)(Ph_3P)_2}$

was shielded from irradiation with aluminum foil, and the other tubes were irradiated with 366 nm (27.3 kcm^{-1}) light. The appropriate gas was passed through each solution, and the irradiated tubes were cooled by a stream of air. The tubes were irradiated for a period of 12 hours, with periodic analysis of samples from each tube by VPC techniques.

Spectral Measurements. Infrared spectra were recorded on a Perkin-Elmer 225 infrared spectrophotometer using KBr pellets prepared from ir spectrograde powder (MC and B), or in 0.1 mm path length NaCl liquid ir cells. Electronic absorption spectra were measured using a Cary 17 spectrophotometer. Spectra at liquid nitrogen temperature were obtained using a low temperature dewar fitted with Suprasil quartz windows, and modified to hold a standard 1.00 cm cell. Emission and excitation spectra were recorded on a Perkin-Elmer MPF-3A fluorescence spectrophotometer fitted with a low temperature unsilvered pyrex dewar.

Results and Discussion

Electronic Absorption Spectra. The electronic absorption spectra of several of the oxidative addition adducts are shown in Figures II-1 - II-7. Although many of these complexes have been known for several years, there has been little attempt at any detailed spectral analysis.[16,17] Since this study is an investigation of the photochemical properties of these complexes, it is necessary to have an understanding of the nature of the excited states populated upon

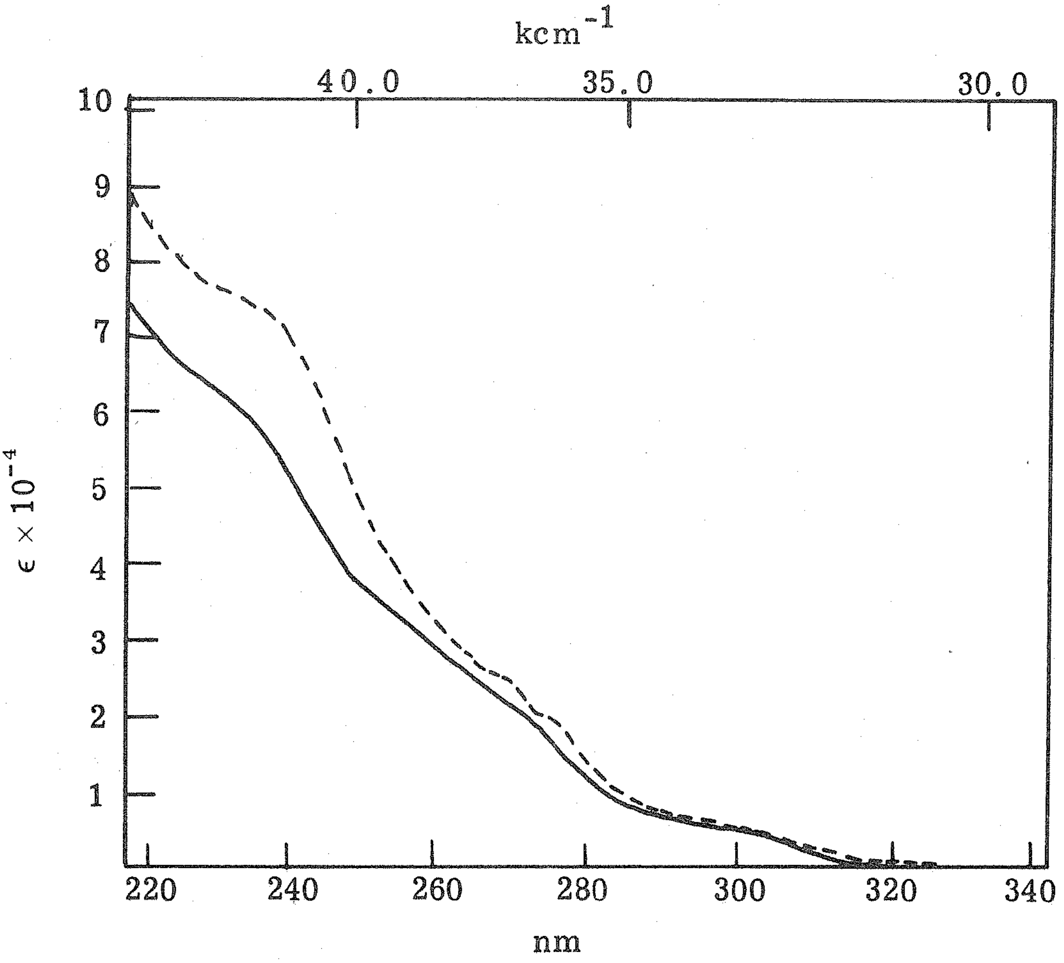


Figure II-1. Electronic spectra of $[Ir(2{=}phos)_2O_2]ClO_4$ in EPA at 300 °K (——) and 78 °K (---).

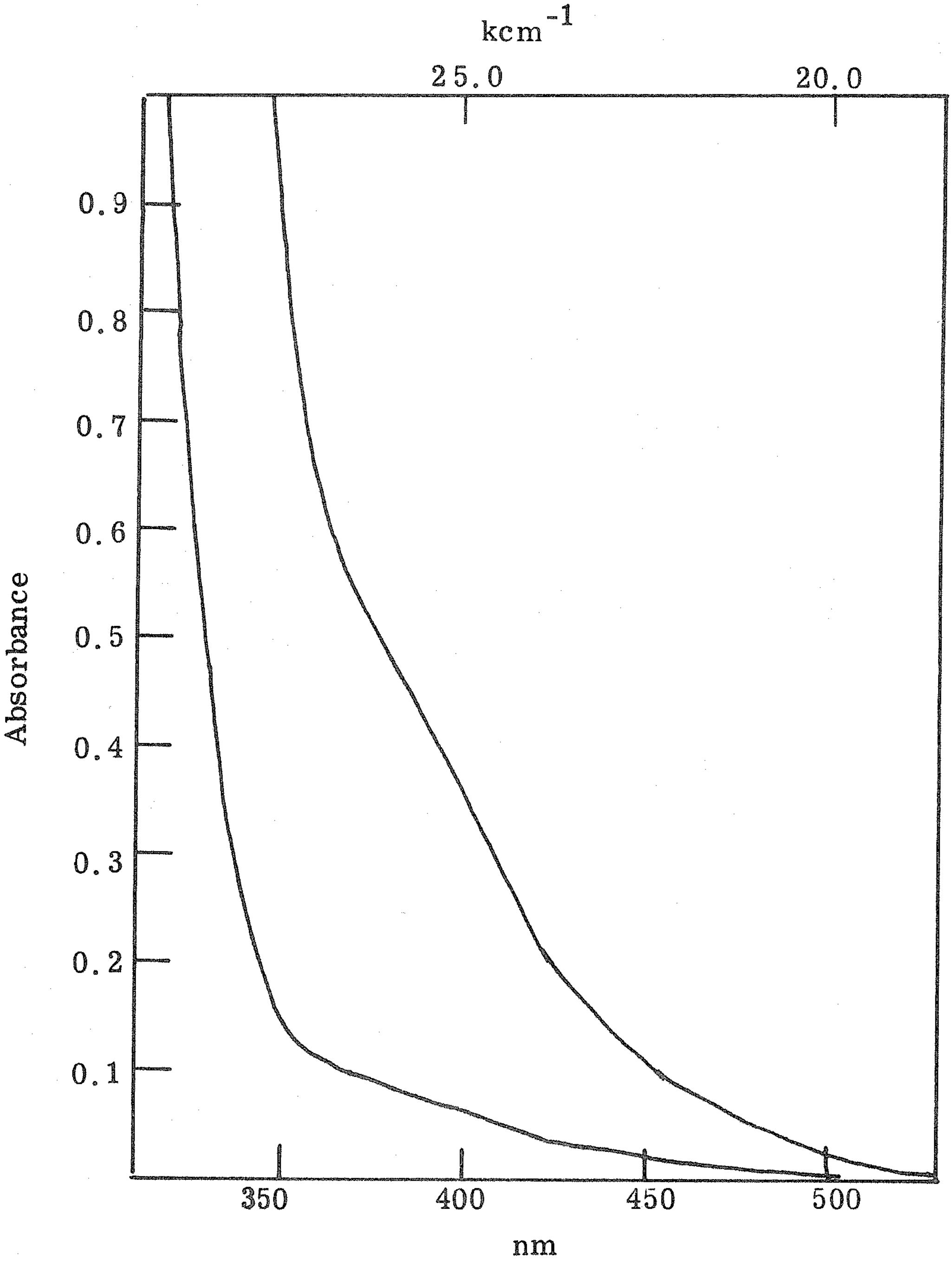


Figure II-2. Electronic spectrum of $[IrO_2(2=phos)_2]Cl$ at two different concentrations in ethanol under an atmosphere of oxygen at 300 °K.

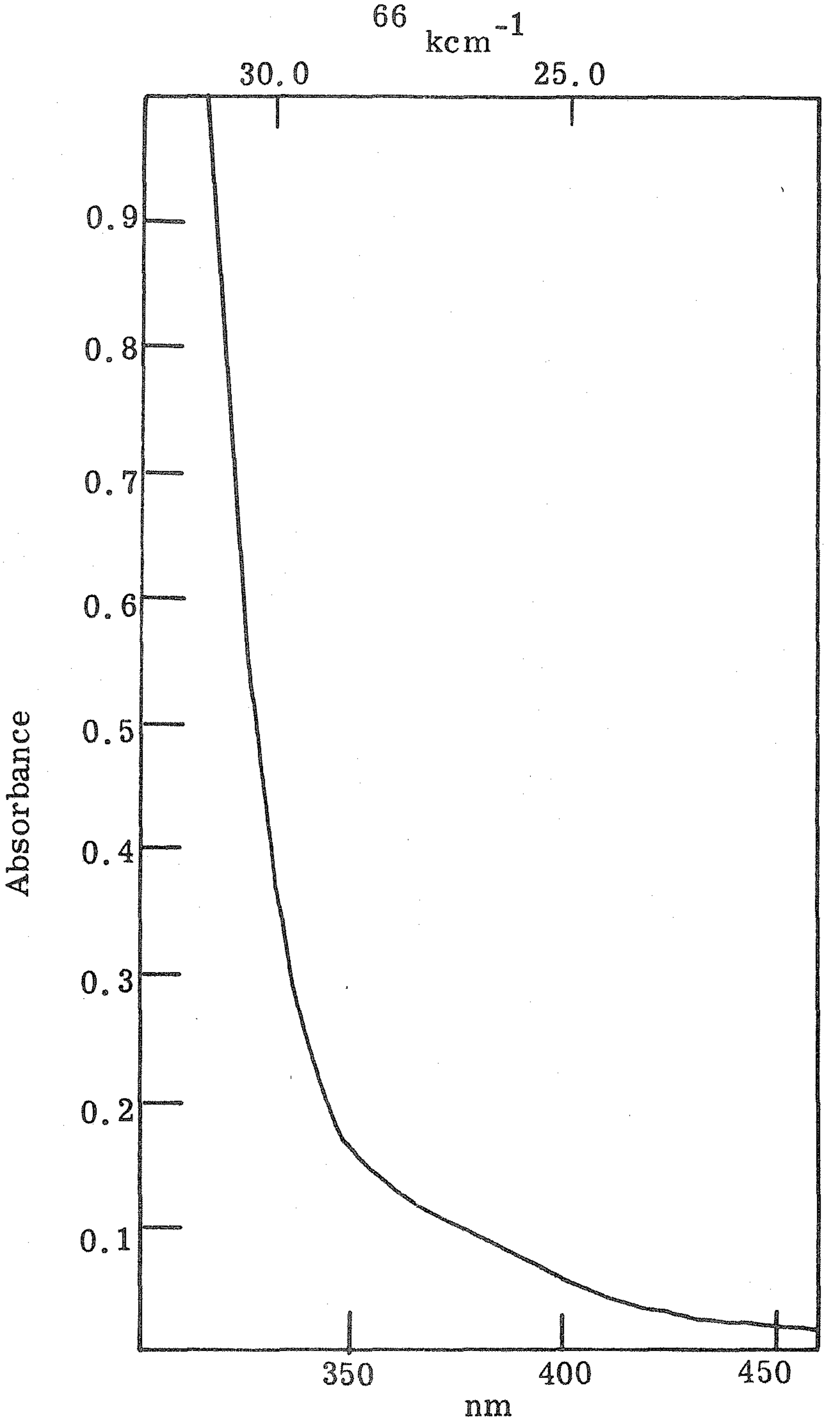


Figure II-3. Electronic spectrum of $[Ir(2\text{-phos})_2H_2]Cl$ in acetonitrile at 300°K.

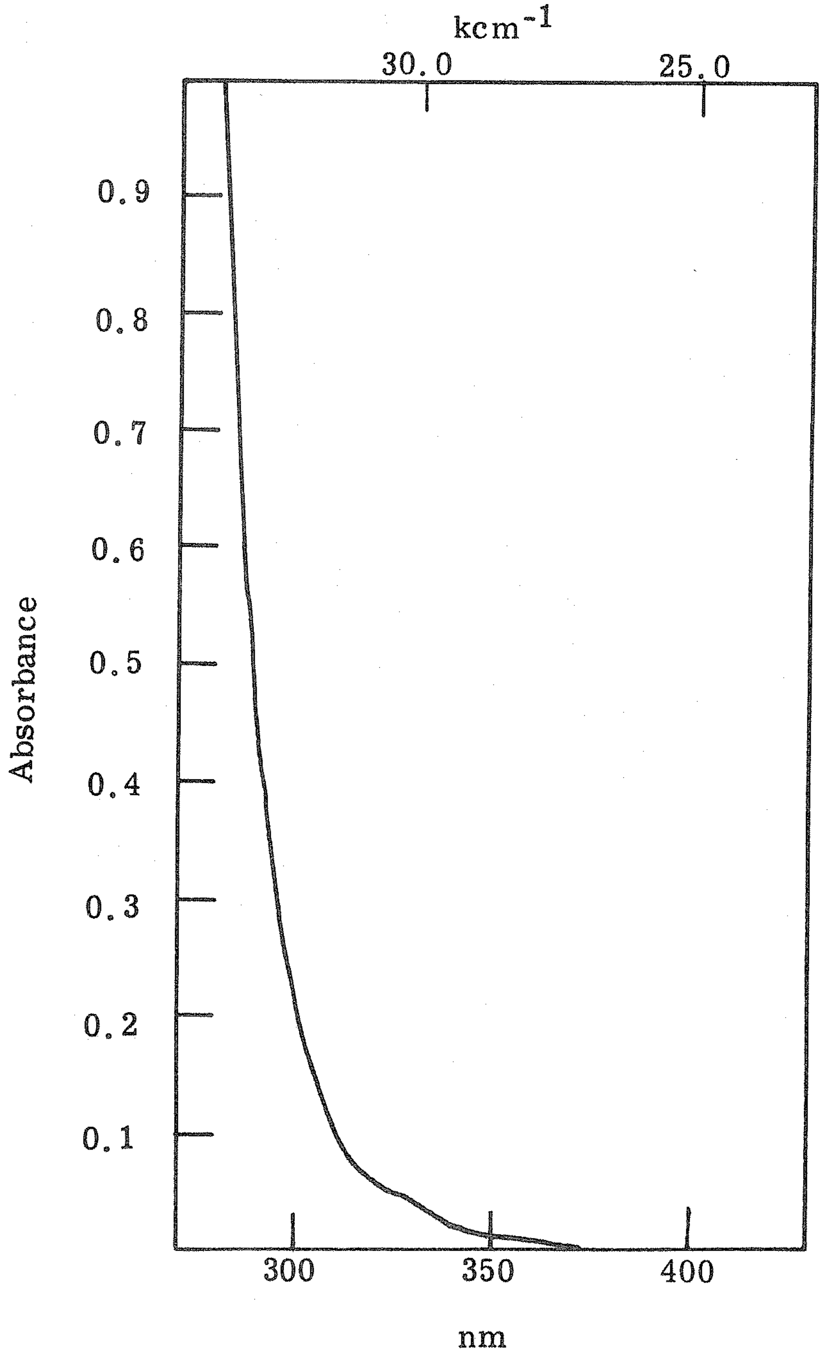


Figure II-4. Electronic spectrum of $[Ir(2\text{=phos})_2H_2]Cl$ in acetonitrile at 300 °K.

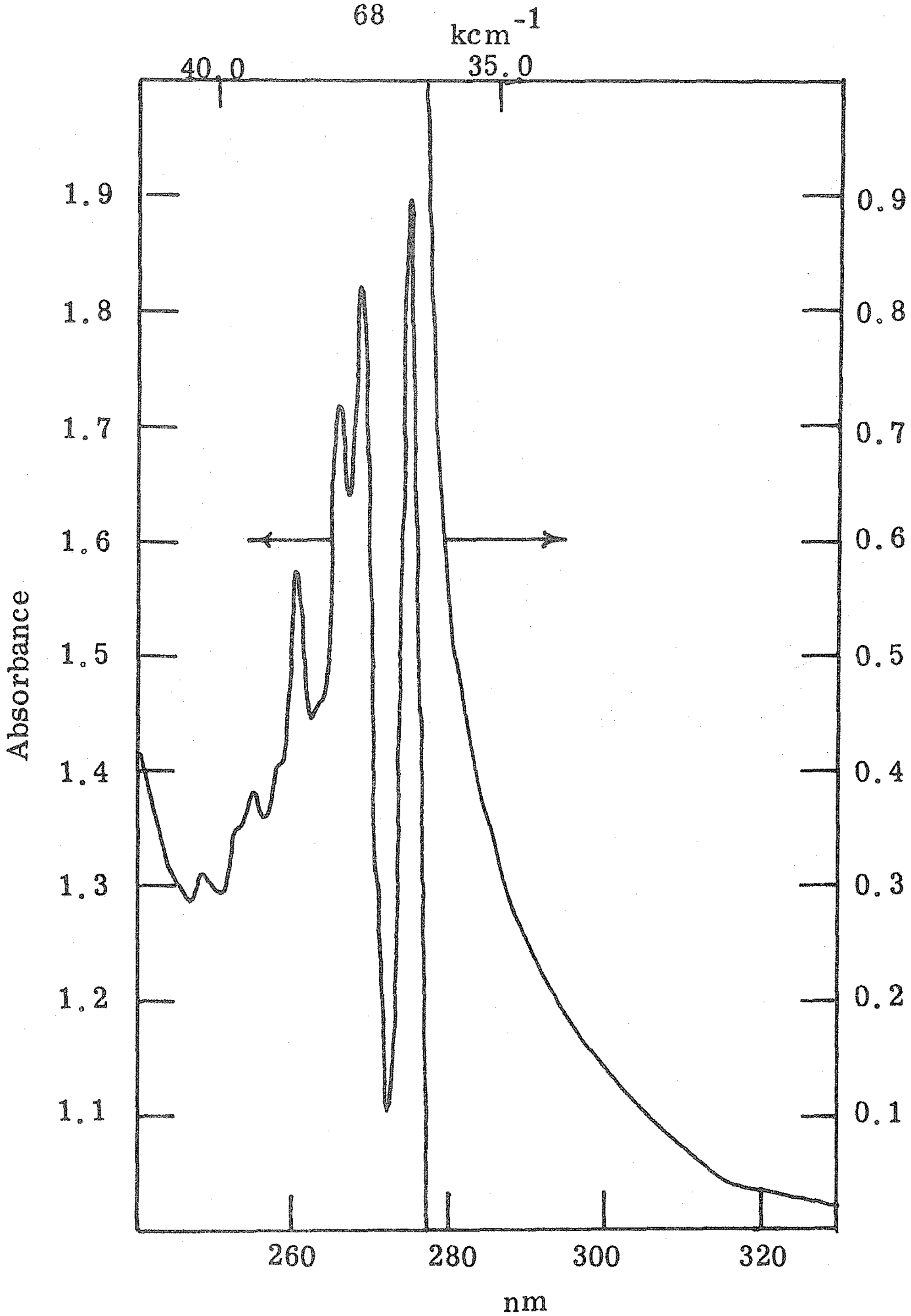


Figure II-5. Electronic spectrum of $Ir(H)_2Cl(CO)(PPh_3)_2$ in acetonitrile solution at 300°K.

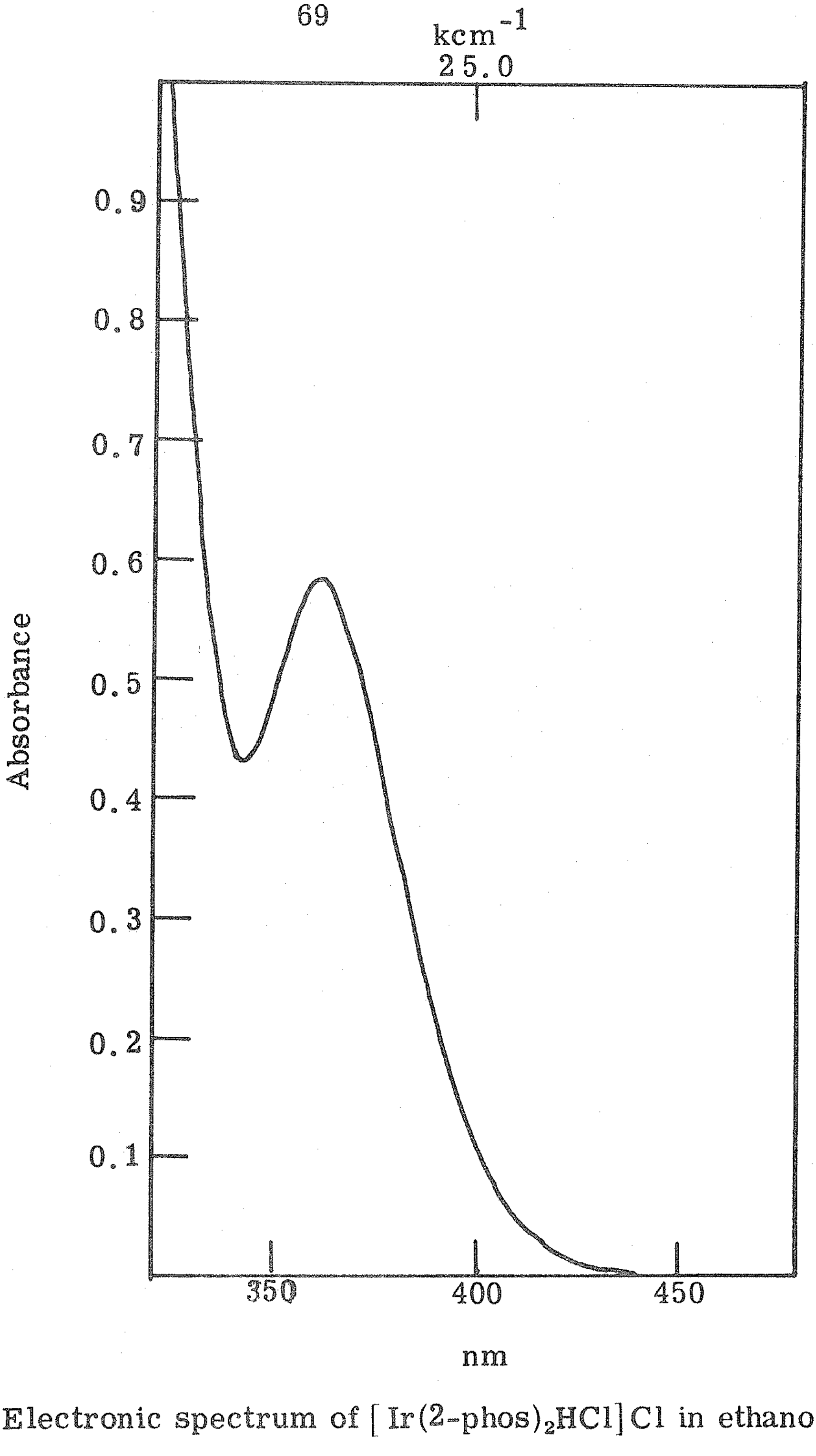


Figure II-6. Electronic spectrum of [Ir(2-phos)$_2$HCl]Cl in ethanol solution at 300 °K.

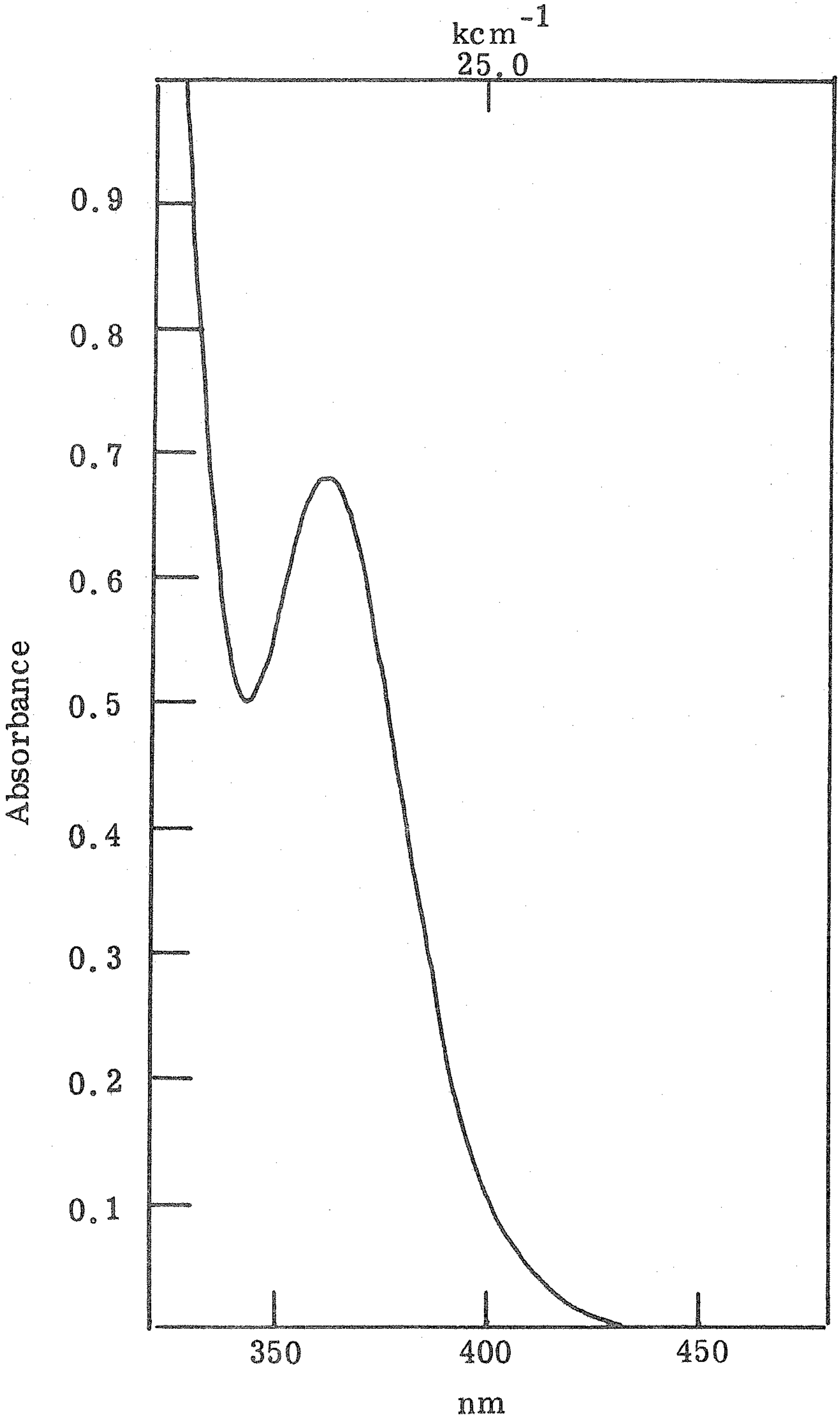


Figure II-7. Electronic spectrum of [Ir(2=phos)$_2$HCl]Cl in ethanol solution at 300°K.

irradiation. Consequently, the absorption spectra were measured with the aim of making definitive band assignments, especially for the least energetic transitions, and of elucidating the nature of the low lying excited states. Unfortunately, the complexity of the spectra (Figures II-1 - II-7) preclude such definitive assignments, and this author will attempt only a brief interpretation.

The spectrum of $[Ir(2\text{=}phos)_2O_2]ClO_4$, shown in Figure II-1, was recently measured and interpreted by Dr. Vince Miskowski of this laboratory.[16] The spectrum shows a shoulder at 33-34 kcm^{-1} ($\epsilon \simeq$ 5000) assigned as the ligand field (LF) $^1A_1 \rightarrow {}^1E^a$ transition,[16,18] and higher energy bands attributed to intraligand (PPh_3) and charge transfer (CF) transitions. The spin-forbidden $^1A_1 \rightarrow {}^3E^a$ transition should be observable at lower energy, but it was not previously identified. This author has measured the spectrum of a concentrated solution of the complex, under an atmosphere of oxygen to insure complete oxygenation, and has observed a low intensity shoulder at about 25.6 kcm^{-1} (Figure II-2). Based on the assignment of $^1A_1 \rightarrow {}^1E^a$ for the 33 - 34 kcm^{-1} band, this weak shoulder is assigned as the $^1A_1 \rightarrow {}^3E^a$ transition, and is most likely the state reached upon 366 nm (27.3 kcm^{-1}) irradiation. $[Ir(2\text{-}phos)_2O_2]^+$ shows a similar shoulder at 26.0 kcm^{-1}, but incomplete oxygenation of $IrCl(CO)(PPh_3)_2$ precluded identification of the analogous transition in $IrCl(CO)(PPh_3)_2O_2$.

Strohmeier and Müller have measured the absorption spectra of a series of $H_2IrX(CO)L_2$ complexes and their data are summarized in Table II-1.[17] In each case they observed a low intensity band at 27.0 - 27.6 kcm^{-1}, but no interpretation of the spectra was given. The electronic absorption spectra of $[H_2Ir(2\text{-phos})_2]Cl$ and $[H_2Ir(2{=}phos)_2]Cl$ in CH_3CN are shown in Figures II-3 and II-4. A weak shoulder is observed at 26.7 kcm^{-1} in the spectrum of $[H_2Ir(2\text{-phos})_2]^+$, and a similar band at 30.3 kcm^{-1} is seen in the 2=phos complex. $H_2IrCl(CO)(PPh_3)_2$ also shows a similar transition at 27.0 kcm^{-1}. These bands are analogous to those reported by Strohmeier and are reminiscent of the $^1A_1 \rightarrow {}^3E^a$ transition observed in the spectra of the oxygen analogs, and may be assigned accordingly. The high energy shoulders and bands in the spectra are most likely intraligand and CT transitions.

Particularly impressive is the richly structured dilute solution spectrum of $H_2IrCl(CO)(PPh_3)_2$ shown in Figure II-5. The structure in this spectrum is very similar to that of the $^1A_{1g} \rightarrow {}^1B_{2u}$ transition in benzene, only more intense.[20] It most likely is such a transition of the triphenylphosphine aromatic rings perturbed by the central phosphorus atom. It is strange that such structure is seen only in the spectrum of this complex and not in the spectra of the other adducts. The spectra of $[HClIr(2\text{-phos})_2]^+$ and $[HClIr(2{=}phos)_2]^+$ are also somewhat unique (Figures II-6 and II-7). Both show a band at 27.8 kcm^{-1} that can be assigned as $^1A_1 \rightarrow {}^3E^a$, but the band is much

Table II-1. Absorption Spectra of a Series of $H_2IrX(CO)L_2$ Complexes in Toluene[a]

Complex	λ_{max} nm	λ_{max} kcm^{-1}	ϵ
$H_2IrBr(CO)[P(C_6H_{11})_3]_2$	365	27.4	38.6
$H_2IrI(CO)[P(C_6H_{11})_3]_2$	370	27.0	34.2
$H_2IrCl(CO)[P(i\text{-}C_3H_7)_3]_2$	362	27.6	35.2
$H_2IrBr(CO)[P(i\text{-}C_3H_7)_3]_2$	365	27.4	6.6
$H_2IrI(CO)[P(i\text{-}C_3H_7)_3]_2$	370	27.0	26.1

[a] Data abstracted from reference 17.

more pronounced than in the H_2 and O_2 adducts. Although these spectra were not quantified, it does appear that the molar extinction coefficients of the bands are significantly greater than in the O_2 and H_2 analogs.

The lowest transition in each of these adducts thus appears to be $^1A_1 \rightarrow {}^3E^a$, based primarily on the assignment of $^1A_1 \rightarrow {}^1E^a$ to the 33 - 34 kcm^{-1} shoulder in the spectrum of $[Ir(2{=}phos)_2O_2]^+$, and on the "reasonableness" of such an assignment. Hence, the excited state populated by 366 nm (27.3 kcm^{-1}) irradiation is most likely the LF $^3E^a$ state. It should, of course, be emphasized that this is by no means a definitive assignment, but only a very attractive one.

Deoxygenation Reactions. Although $IrCl(CO)(PPh_3)_2O_2$ loses O_2 when solutions of the complex are purged with inert gas, the deoxygenation does not spontaneously proceed in the absence of a purge. In air saturated solutions, the equilibrium in Eq. 2

$$IrCl(CO)(PPh_3)_2O_2 \rightleftharpoons IrCl(CO)(PPh_3)_2 + O_2 \qquad (2)$$

lies far to the left, and yellow solutions of $IrCl(CO)(PPh_3)_2$ slowly add oxygen from room air to give colorless solutions of the O_2 adduct. Irradiation of air saturated solutions of $IrCl(CO)(PPh_3)_2O_2$, however, does induce loss of oxygen and regeneration of the square planar species. This photoinduced deoxygenation can be followed spectrophotometrically, and spectral changes which occur during the irradiation of a benzene solution of the oxygen complex are shown in Figure II-8. As the photolysis proceeds, the 22.7, 25.8, and 29.5 kcm^{-1} bands of

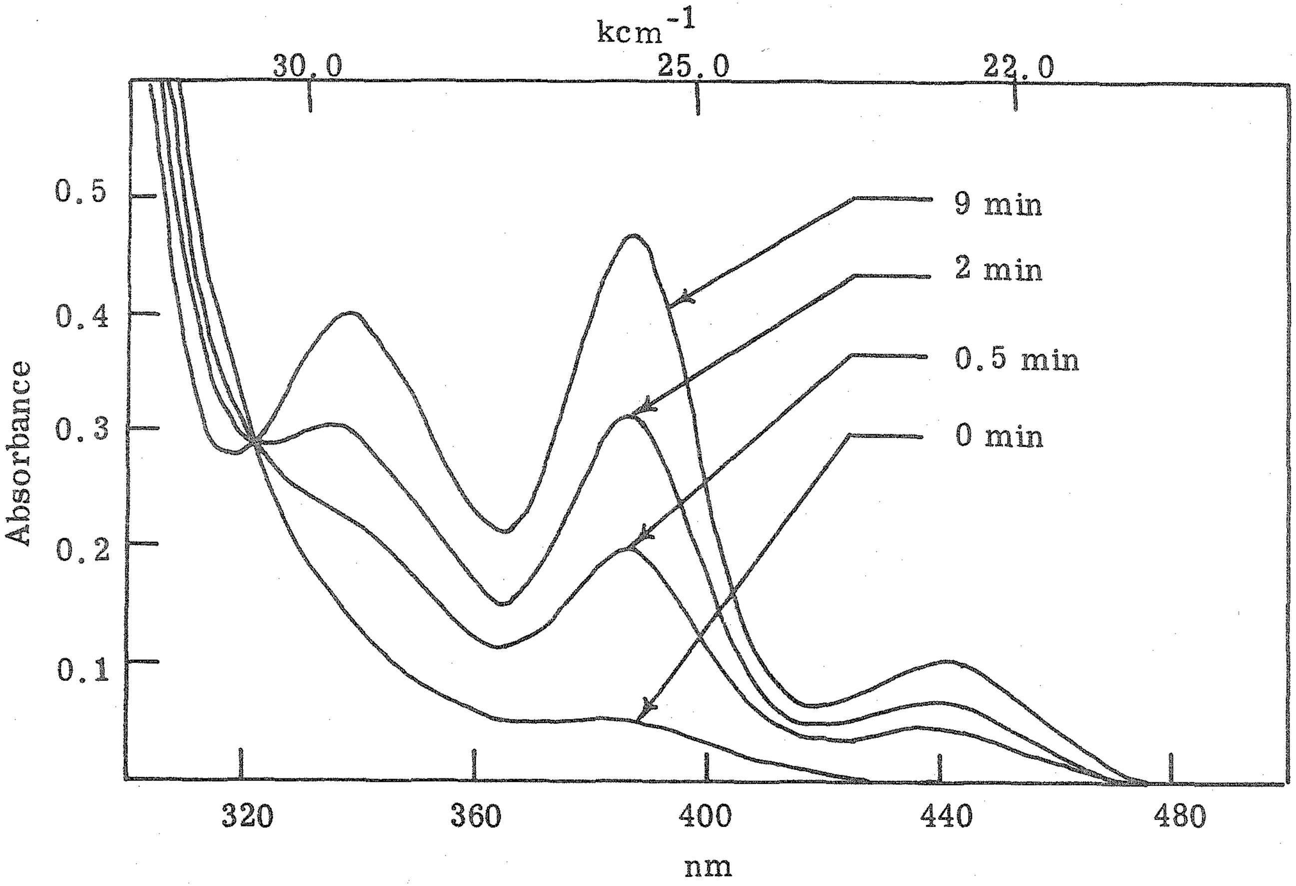


Figure II-8. Spectral changes during 366 nm (27.3 kcm^{-1}) irradiation of $IrO_2Cl(CO)(PPh_3)_2$ in benzene.

$IrCl(CO)(PPh_3)_2$ grow in, with the isosbestic point indicating a smooth conversion to a single product. Even in air saturated solutions the deoxygenation reaction can be made to go to completion, and the thermal oxygenation-photochemical deoxygenation reactions can be cycled several times without noticable decomposition of the complex.

In the absence of oxygen, the square planar complex itself does not appear to be photosensitive. Although some decomposition does occur upon very prolonged photolysis, it is not fast and is a low quantum yield process. The carbonyl stretching frequency should be very sensitive to any changes in the nature of the complex, and irradiation of $IrCl(CO)(PPh_3)_2$ in benzene and in toluene with and without an excess of PPh_3 has been monitored in the ir. In neither case is there a noticeable change in the carbonyl stretching frequency or intensity, indicating that no photoreaction occurs. Irradiation of the square planar complex under an oxygen purge, however, does result in noticeable decomposition. Irradiation of $IrCl(CO)(PPh_3)_2$ in benzene under oxygen for 20 h with 366 nm (27.3 kcm^{-1}) produced a green solution with the absorption spectrum shown in Figure II-9. A control solution which was purged with oxygen but kept in the dark gave only the $IrCl(CO)(PPh_3)_2O_2$ spectrum. Both solutions were evaporated to dryness and ir spectra of the green tar from the irradiated sample and of the yellow solid from the dark sample were recorded. The green substance showed ir peaks at 2015, 1955, 1190 and 1115 cm^{-1}, among others, and the yellow solid showed a single peak (plus coordinated PPh_3 bands) at 2015 cm^{-1}. The 2015 cm^{-1} peak is

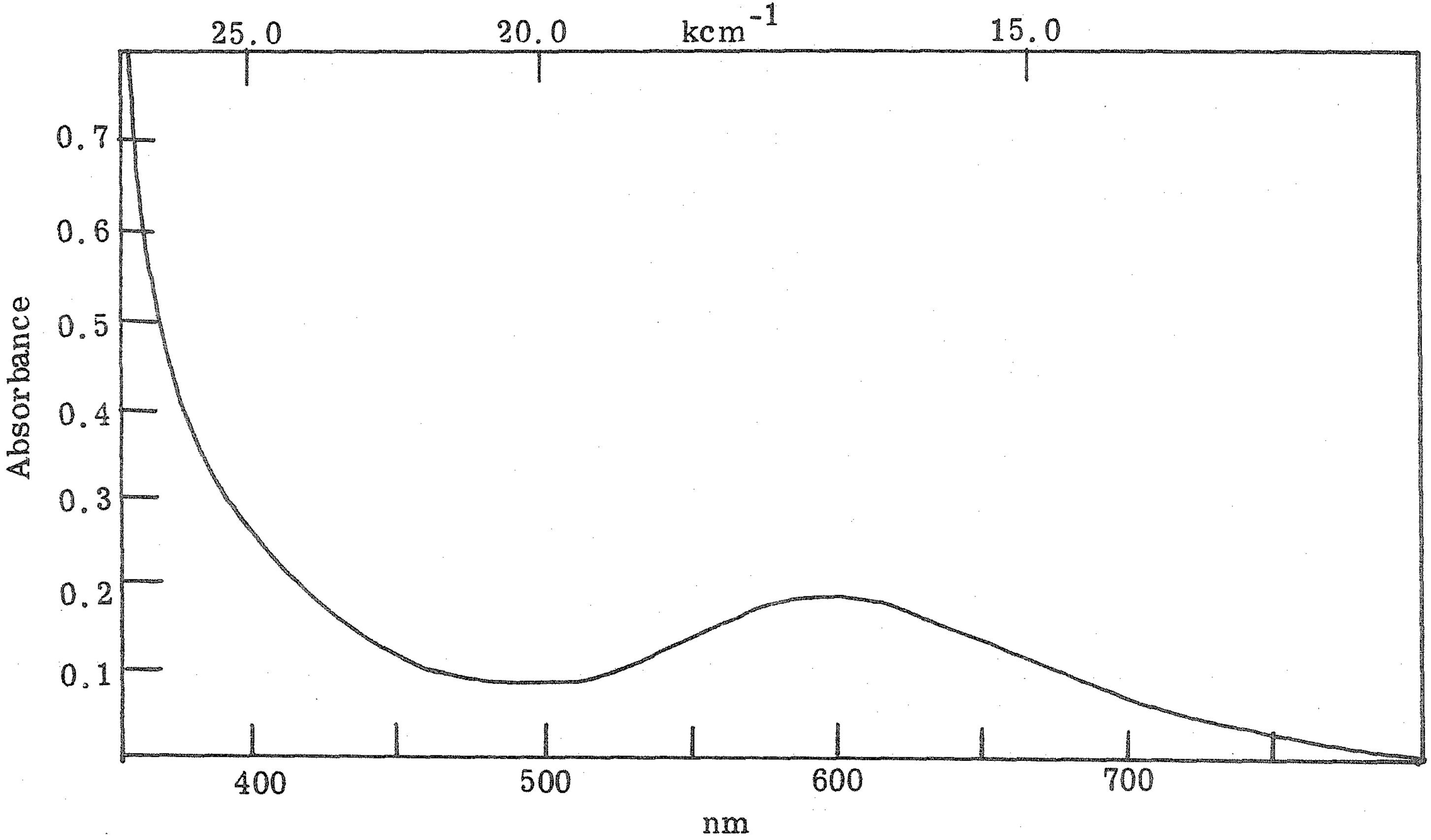


Figure II-9. Electronic spectrum of the green benzene solution from 366 nm (27.3 kcm^{-1}) irradiation of $IrCl(CO)(PPh_3)_2$ under an oxygen purge.

attributable to the oxygen adduct[1] and the 1955 cm^{-1} band is probably a CO stretch of some unknown Ir complex (not $IrCl(CO)(PPh_3)_2$ which shows a single stretch at 1967 cm^{-1}[1]). The 1190 and 1115 cm^{-1} bands, which are absent in $IrCl(CO)(PPh_3)_2$, can be assigned as $\nu_{P=O}$ and are strongly indicative of $Ph_3P{=}O$. The 1190 cm^{-1} peak is very close to the 1195 cm^{-1} stretch observed in free $Ph_3P{=}O$,[21] and the 1115 cm^{-1} peak can be attributed to coordinated $Ph_3P{=}O$, as coordination is known to shift $\nu_{P=O}$ to lower energy, usually by 50 - 60 cm^{-1}.[21] The band at 16.4 kcm^{-1} in the electronic absorption spectrum of the green solution (Figure II-9) is somewhat of a mystery. Presumably, it is due to an iridium species, as it is doubtful that any organic product would have spectral features at such low energy. Since transitions in Ir(I) and Ir(III) complexes are expected at much higher energy, it is attractive to postulate an Ir(IV) complex. This is consistent with observations by Jorgensen of weak bands at 16.0 kcm^{-1} ($\epsilon = 460$) and 17.4 kcm^{-1} ($\epsilon = 400$) in $Irpy(Cl)_5^-$ and $Ir(Cl)_6^{2-}$, respectively, which he attributed to chloride to Ir(IV) charge transfer.[22] It thus appears that the irradiated solution contains $IrCl(CO)(PPh_3)_2O_2$, free $PPh_3 = O$, coordinated $PPh_3 = O$, and an Ir(IV) complex, and it is attractive to speculate that irradiation of $IrCl(CO)(PPh_3)_2$ in the presence of O_2 results in the formation of an Ir(IV)-triphenylphosphine oxide complex. Of course, this is exactly what Vaska proposed in his earlier observations.[4]

$IrICO(PPh_3)_2O_2$, which binds oxygen much more strongly than the chloride analog and cannot be readily deoxygenated thermally,[1,10] undergoes photochemical reactions very similar to those described above. Spectral changes indicate that irradiation of the adduct does induce deoxygenation and regeneration of $IrI(CO)(PPh_3)_2$. However, the square-planar complex itself is quite photosensitive and rapidly decomposes when irradiated in solution. Consequently, the deoxygenation cannot be made to go to completion, and the oxygenation-deoxygenation reactions cannot be cycled. The photosensitivity of the complex is not altogether surprising as I^- complexes are notorious for giving I· upon photolysis.

The most significant deoxygenation reactions are those of $[Ir(2\text{-phos})_2O_2]^+$ and $[Ir(2{=}phos)_2O_2]^+$. These complexes have long been considered "irreversible," and the O-O distance in $[Ir(2\text{-phos})_2O_2]^+$ has been shown by X-ray crystallography to be the longest in the entire series of Ir(I)-oxygen adducts.[23] The long O-O distance is indicative of a very strong $Ir-O_2$ bond. Yet photolysis of each of these adducts does induce deoxygenation, as evidenced by the spectral changes shown in Figure II-10. It must be noted that unlike $IrCl(CO)(PPh_3)_2O_2$, the deoxygenation cannot be observed to any great extent unless solutions are purged with an inert gas during the photolysis. The oxygenation reaction is so fast that unless the photo-released O_2 is swept out of solution, the complexes will reoxygenate. The deoxygenation reaction can be made to go to completion and the systems can be cycled

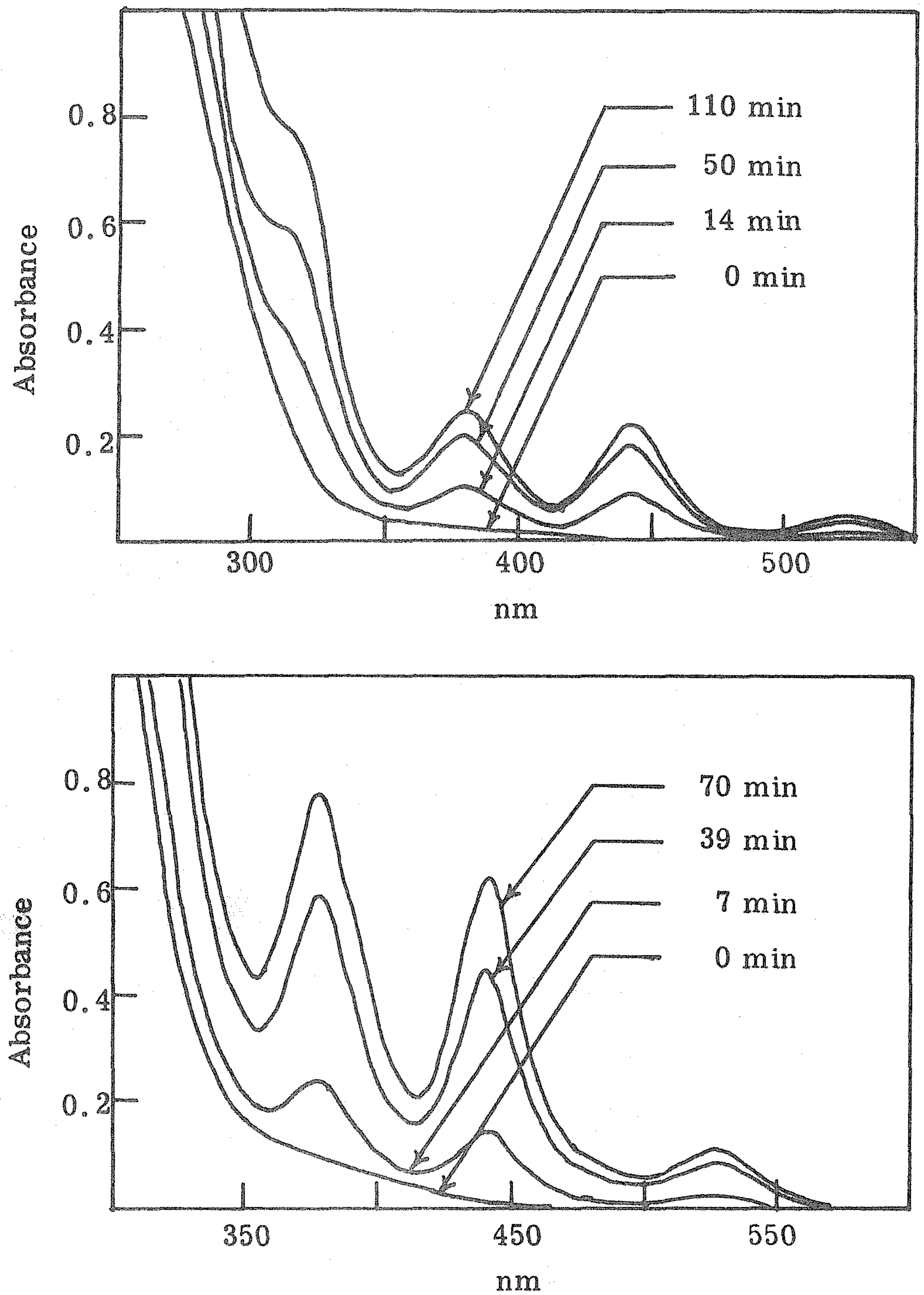
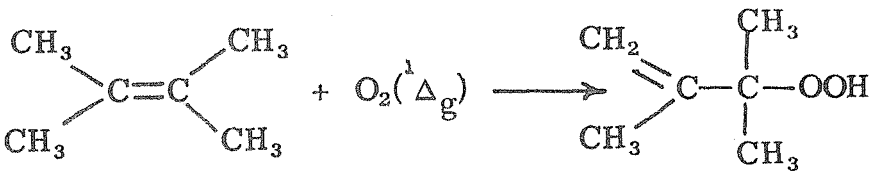


Figure II-10. Spectral changes during 366 nm (27.3 kcm^{-1}) irradiation of ethanol solutions of a) [Ir(2-phos)$_2$O$_2$]Cl and b) [Ir(2=phos)$_2$O$_2$]Cl.

indefinitely. The square planar complexes appear to be completely insensitive to irradiation, as prolonged photolysis, even in the presence of oxygen, does not lead to decomposition. These results have some practical utility, as prior to this study very severe conditions were required to regenerate the square planar species once oxygenation had occurred.[24] This study shows that under mild photochemical conditions the square planar compounds can be regenerated in solution and used for further studies.

Interestingly, irradiation of $[Co(2\text{=}phos)_2O_2]^+$ does not induce deoxygenation. Ligand field irradiation (22.9 kcm^{-1}) of solutions of this complex gives no detectable reaction, even with a strong inert gas purge. However, charge transfer irradiation (27.3 kcm^{-1}) does induce decomposition of the complex but not regeneration of $[Co(2\text{=}phos)_2]^+$. The spectral changes occurring during CT photolysis are very complex, and no isosbestic points are maintained.

Experiments have been performed to determine if the oxygen released when the O_2 adducts are irradiated is in the $^1\Delta_g$ excited state. Foote has shown that $O_2(^1\Delta_g)$ reacts with tetramethylethylene (TME) to give the reaction shown below (Eq. 3).[25]



(3)

The peroxide can be reduced to 2, 3-dimethyl-3-hydroxy-1-butene by BH_4^-, and the alcohol can be detected by VPC techniques. Solutions of $[Ir(2\text{-phos})_2O_2]^+$ and $[IrCl(CO)(PPh_3)_2O_2]$ have been irradiated in the presence of TME, with and without an oxygen purge, and the solutions reduced by BH_4^-. In no case were quantities of 2, 3-dimethyl-3-hydroxy-4-butene detected greater than the very small amount found in control experiments. These results, then, indicate that $O_2(^1\Delta_g)$ is not formed in the photo-induced deoxygenation reactions.

Dehydrogenation and Dehydrochloronation Reactions. As is the case with oxygen, H_2 forms a stable "reversible" adduct with $IrCl(CO)(PPh_3)_2$.[1] The product, $H_2IrCl(CO)(PPh_3)_2$, is probably best viewed as an Ir(III)-dihydride complex. When solutions of the adduct are purged with an inert gas, reductive elimination occurs and H_2 is lost. Irradiation of purged solutions of the adduct markedly enhances the rate of dehydrogenation, but, unlike the O_2 adduct, no photochemical reductive elimination is observed in the absence of a purge. The rate of dehydrogenation of an irradiated and purged solution of $H_2IrCl(CO)(PPh_3)_2$ was found to be 2.6 times the rate of dehydrogenation of a purged solution kept in the dark (Figure II-11). The rate of purge was identical in both samples. Ir(I)(CO(PPh$_3$)$_2$ forms an "irreversible" H_2 adduct, but when solutions of the adduct are irradiated and purged, loss of H_2 occurs and the square planar complex is regenerated. Again, this latter species is photosensitive and rapidly decomposes under the influence of light.

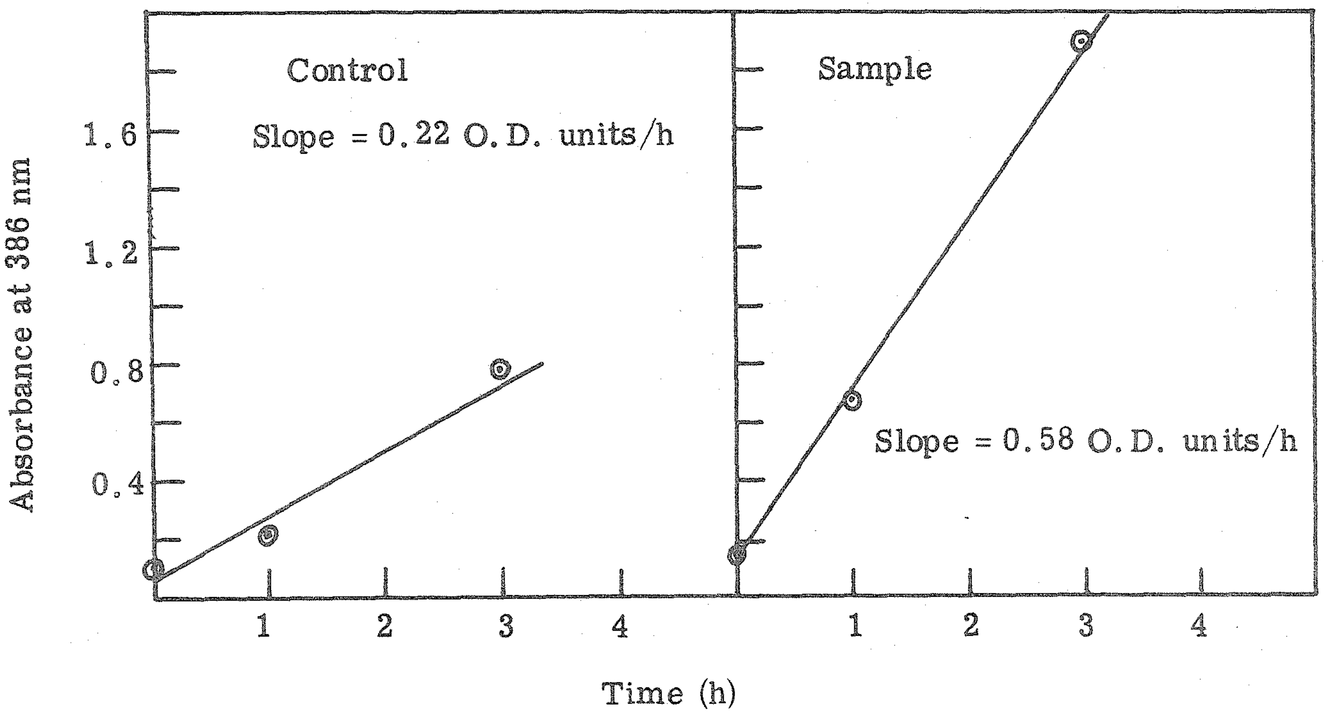
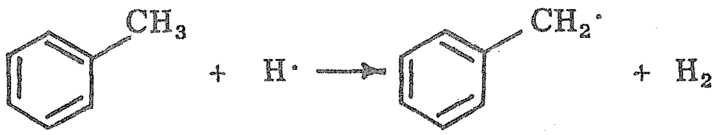


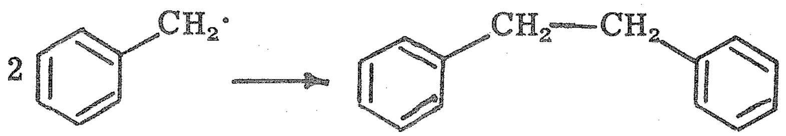
Figure II-11. Plot of absorbance at 386 nm versus time for control (dark) and 366 nm (27.3 kcm^{-1}) irradiated solutions of $Ir(H)_2Cl(CO)(PPh_3)_2$ in benzene. Ratio of photochemical rate to thermal rate = 0.58/0.22 = 2.6.

Dehydrogenation of the "irreversible" adducts $[H_2Ir(2\text{-phos})_2]^+$ and $[H_2Ir(2{=}phos)_2]^+$ can also be induced by irradiation of purged solutions. The dehydrogenation can be made to go to completion and the systems can be cycled many times. Although 366 nm (27.3 kcm^{-1}) irradiation is effective in causing dehydrogenation of $[H_2Ir(2\text{-phos})_2]^+$, it will not induce loss of H_2 from $[H_2Ir(2{=}phos)_2]^+$. However, dehydrogenation of the latter complex does occur with 313 nm (31.9 kcm^{-1}) or 254 nm (39.4 kcm^{-1}) irradiation. This observation is consistent with the electronic absorption spectra of the H_2 adducts shown in Figures II-3 and II-4. The low energy shoulder $({}^1A_1 \rightarrow {}^3E^a)$ in $[H_2Ir(2\text{-phos})_2]^+$ is at 26.7 kcm^{-1}, whereas it is at 30.3 kcm^{-1} in $[H_2Ir(2{=}phos)_2]^+$. Hence, in the 2=phos complex it is necessary to use higher energy irradiation to reach the active excited state.

The mechanism of dehydrogenation is of interest as several possibilities exist. Hydrogen can leave the complex in a concerted fashion to give H_2 directly, or one hydrogen can be expelled as $H^\cdot$ or H^-, followed by loss of the other hydrogen as $H\cdot$ or H^+ and subsequent combination to give H_2. Toluene is an effective scavenger of hydrogen atoms, giving the following reactions (Eq. 4-5):



(4)



(5)

Irradiation of $[H_2Ir(2\text{-phos})_2]^+$ in toluene under an H_2 purge was found not to lead to the formation of dibenzyl, indicating that H· is not formed in the photolysis. No experiment has been performed to test for H^-.

Hydrogen chloride reacts with $IrCl(CO)(PPh_3)_2$, $[Ir(2\text{-phos})_2]^+$, and $[Ir(2{=}phos)_2]^+$ to give stable, irreversible HCl adducts, which must be considered as H^- and Cl^- complexes of Ir(III). Surprisingly, irradiation of purged solutions of $(H)(Cl)IrCl(CO)(PPh_3)_2$ induces loss of HCl and regeneration of $IrCl(CO)(PPh_3)_2$! The dehydrochlorination reaction can be made to go to completion with continued photolysis, and the rate of dehydrochlorination is about one-fifth the rate of dehydrogenation under similar experimental conditions. This reductive elimination reaction is quite significant since HCl is strongly bound to the metal. It is interesting to consider the large number of Ir(III) and Rh(III) complexes that should be investigated to see if they also undergo this type of photochemical induced reductive elimination. For example, it is conceivable that irradiation of $Rh(Cl)_3CO(PPh_3)_2$ could lead to loss of Cl_2 and formation of $Rh(Cl)(CO)(PPh_3)_2$.

Unfortunately, irradiation of purged solutions of $[(H)(Cl)Ir(2\text{-phos})_2]^+$ and $[(H)(Cl)Ir(2{=}phos)_2]^+$ does not lead to regeneration of $[Ir(2\text{-phos})_2]^+$ and $[Ir(2{=}phos)_2]^+$. However, there is a photochemical reaction as evidenced by the electronic absorption spectral changes shown in Figure II-12, but it is not clear what chemical changes occur.

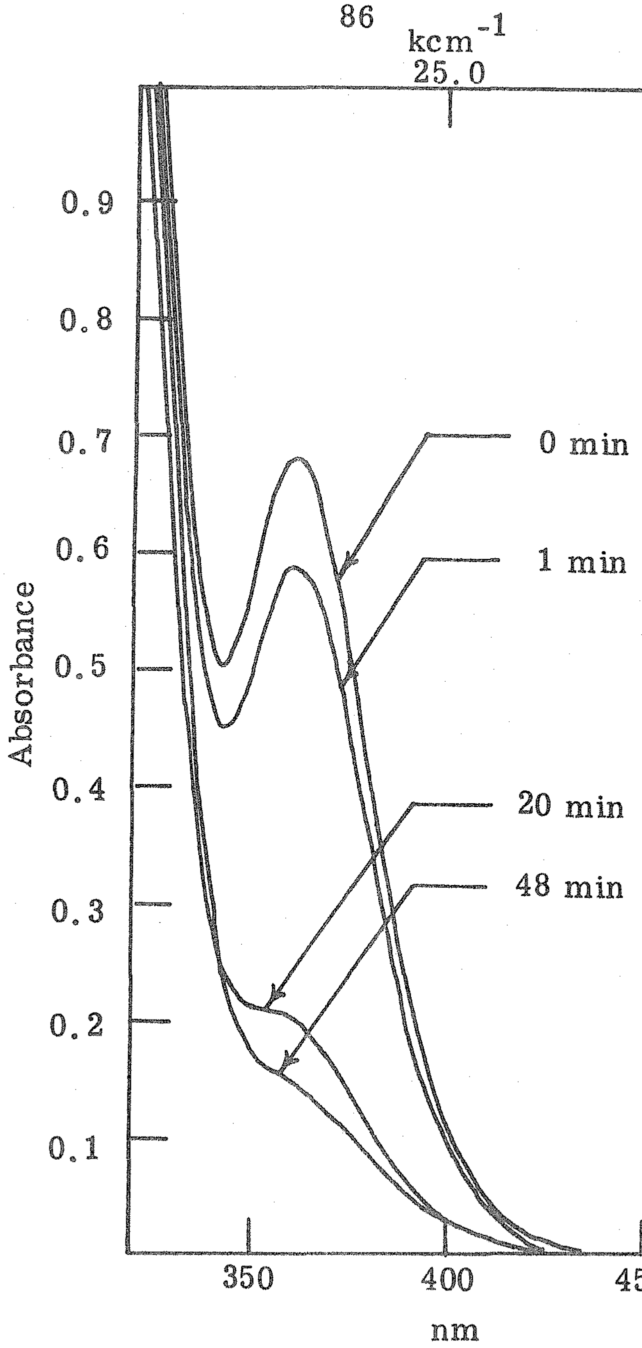


Figure II-12. Spectral changes during 366 nm (27.3 kcm^{-1}) irradiation of [Ir(2=phos)$_2$HCl]Cl in ethanol solution at 300 °K.

Low Temperature Photolysis. Interesting phenomena occur when these many adducts are irradiated at 77°K in an EPA glass. The irradiations are conducted through a clear pyrex dewar filled with liquid nitrogen, and all but a small area is masked off so that light reaches only a well defined area of the sample tube. When the H_2 and O_2 adducts of $IrCl(CO)(PPh_3)_2$ are photolyzed, the portion of the sample that is irradiated undergoes a color change from colorless to yellow. The yellow color is that of $IrCl(CO)(PPh_3)_2$, and thus the reductive-elimination reactions can also be induced in a solid matrix at 77°K. When the sample is allowed to warm to room temperature, the color persists in solution, but then slowly disappears as oxygenation or hydrogenation occurs.

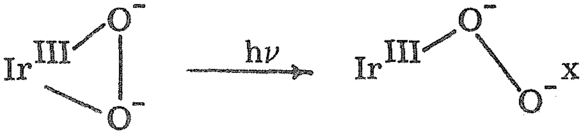
The chemistry is slightly different with the O_2 and H_2 adducts of $[Ir(2\text{-phos})_2]^+$ and $[Ir(2{=}phos)_2]^+$. If the samples are immersed in liquid nitrogen (LN_2) during the photolysis, there is no color change in the irradiated area. However, if the sample is removed from the LN_2 after the irradiation, and allowed to warm slightly(not so much as to melt the glass), the irradiated area turns the bright orange color of the square planar complexes. If the sample is then cooled again to 77°K, the orange coloration persists and the sample shows the characteristic emission spectrum of the square planar complex.[26] These results can be interpreted by assuming that in the rigid glass at 77°K, the photo-induced reductive elimination reaction occurs, but that the rigid media prohibits the bent iridium-ligand system from relaxing to square planar geometry. As soon as the glass warms slightly and softens, the complex relaxes to the stable planar form and the orange color appears.

Photocatalytic Study. One of the original goals of this study was to find a photocatalytic oxygenation or hydrogenation system. Consequently, $IrCl(CO)(PPh_3)_2$ was irradiated in the presence of unsaturated substrate under an oxygen or hydrogen purge, and solutions were analyzed for oxidation or hydrogenation products by VPC techniques. The substrates chosen were tetramethylethylene and 1-hexene, and in each study two control experiments were performed. In addition to the benzene solution of $IrCl(CO)(PPh_3)_2$ and substrate, a solution containing only substrate was irradiated, and a second control solution of $IrCl(CO)(PPh_3)_2$ and substrate was shielded from irradiation. Each solution was purged with a stream of O_2 or H_2, as appropriate, and the rate of purge was identical in each tube. Unfortunately, no hydrogenation products were observed in any of the experiments, and although a small amount of oxygenation products were found, they were never in greater quantity in the irradiated $IrCl(CO)(PPh_3)_2$ solution than in the control solution. It can thus be concluded that, at least with these types of substrates, no photocatalytic hydrogenation or oxygenation effects exist.

Mechanistic Considerations. The nature of the excited states which lead to the observed reductive elimination reactions in these adducts is of considerable interest. Spectral evidence presented earlier suggests that the lowest excited state in each adduct is a LF $^3E^a$ state. LF states are often known to give substitution chemistry, generally by simple expulsion of a ligand with no net change in the oxidation state of that ligand. For example, LF irradiation of $[Ir(CN)_5Br]^{3-}$ gives the aquo complex and Br^- (Eq. 6):[27]

$$[Ir(CN)_5Br]^{3-} \xrightarrow[H_2O]{h\nu} [Ir(CN)_5H_2O]^{2-} + Br^- \qquad (6)$$

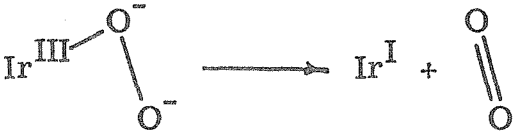
If the coordinated oxygen in $[Ir(2\text{-phos})_2O_2]^+$ and the other oxygen adducts are formulated as O_2^{2-}, then LF irradiation is predicted to give the reaction (Eq. 7):



I

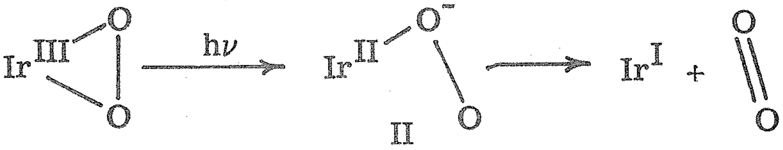
(7)

To obtain the final products, the intermediate I would have to undergo the following reaction, giving two electrons back to the central metal (Eq. 8):



(8)

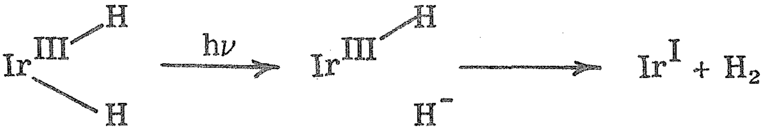
Such a process seems rather unlikely. However, if the active state in each complex is LMCT in nature, then the following process would be predicted (Eq. 9):



(9)

The Ir(II) intermediate formed in this reaction should be very unstable and rapidly decompose into the Ir(I) complex and molecular oxygen. Although the CT mechanism seems more probable than the LF scheme, the available spectral evidence does not indicate that a LMCT (O_2^{2-} → Ir(III)) state is populated upon irradiation. Such a LMCT transition was not observed in the spectrum of either $[Co(2\text{=phos})_2O_2]^+$ or $[Ir(2\text{=phos})_2O_2]^+$.[16] It is most likely that a LF state is indeed the active state, but that the complex cannot be simply formulated as containing Ir(III) and O_2^{2-}. It is conceivable that as one end of the coordinated oxygen is expelled from a LF state, simultaneous electron flow occurs, the intermediate II in Eq. 9 is reached, and this intermediate then decomposes into the products.

An active LF state is consistent with the observed photochemistry of the dihydride complexes in which excitation would lead to the reaction in Eq. 10:



(10)

In this mechanism the photoexpelled H^- extracts a proton from the Ir(III) intermediate to give H_2 and the Ir(I) complex. LMCT irradiation would be expected to produce $H^\cdot$, a species not detected in the reaction.

Unfortunately, at this time little more can be said concerning the mechanism of the photoinduced reductive elimination reaction. One possibility, not mentioned above, is that the small molecule leaves the complex in a concerted fashion giving the square planar species and the free molecule directly, without proceeding through an intermediate. The mechanism of the oxidative-addition reactions of these Ir(I) species is not clearly understood either. In some cases it appears that a concerted addition occurs,[28] and in other cases a free radical process is indicated.[29]

Extension of this Study

This study has shown that irradiation of "irreversible" O_2, H_2, and in one case, HCl adducts can lead to photoinduced reductive-elimination with generation of stable coordinatively unsaturated Ir(I) complexes. These results suggest that it would be extremely interesting to investigate the photochemical properties of other types of complexes where such reductive-elimination could lead to unstable, very reactive species. For example, irradiation of $RuH_2(PPh_3)_4$ might lead to reductive elimination and formation of H_2 and an unstable, four-coordinate Ru(0) complex (Eq. 11):

$$RuH_2(PPh_3)_4 \xrightarrow{h\nu} Ru(PPh_3)_4 + H_2 \qquad (11)$$

This type of photoreaction could thus provide a unique pathway for formation of reactive complexes.

One possible application of this study has been communicated by the author to Dr. Al Ginsberg, who has prepared S_2 and Se_2 adducts of $[Ir(2\text{-phos})_2]^+$.[30] Dr. Ginsberg has tried without success to effect removal of the small molecules from the adducts once they are formed.[31] The results presented herein strongly suggest that irradiation of the S_2 and Se_2 adducts could effect the reductive-elimination.

References

1. L. Vaska, Accounts Chem. Res., 1, 335 (1968).
2. L. Vaska and J. W. Diluzio, J. Amer. Chem. Soc., 83, 2784 (1961).
3. L. Vaska and J. W. Diluzio, J. Amer. Chem. Soc., 84, 679 (1962).
4. L. Vaska, Science, 140, 809 (1963).
5. L. Vaska and S. S. Bath, J. Amer. Chem. Soc., 88, 1333 (1966).
6. L. Vaska and R. E. Rhodes, J. Amer. Chem. Soc., 87, 4970 (1965).
7. L. Vaska, Science, 152, 769 (1966).
8. L. Vaska and D. L. Eatone, J. Amer. Chem. Soc., 88, 5324 (1966).
9. L. Vaska, L. S. Chen, and W. V. Miller, J. Amer. Chem. Soc., 93, 6671 (1971).
10. J. A. McGinnety, R. J. Doedens, and J. A. Ibers, Inorg. Chem., 6, 2243 (1967).
11. L. Vaska, "Proc. IX I.C.C.C., St. Moritz," p. 332, 1966.
12. S. Doronzo and V. D. Bianco, Inorg. Chem., 11, 466 (1972).
13. L. Vaska, J. Amer. Chem. Soc., 88, 5325 (1966).
14. 2-phos is 1,2-bis(diphenylphosphino)ethane; 2=phos is 1,2-bis-(diphenylphosphino)ethylene.
15. D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, 1969.

16. Vincent M. Miskowski, Ph.D. Thesis, California Institute of Technology, 1973.

17. W. Strohmeier and F. J. Müller, *Z. Naturforsch.*, **1324**, 770 (1969).

18. Such an assignment was made by assuming a d^6-Ir(III) central metal. Although the *cis* octahedral complexes have only C_{2v} symmetry, the $^1A_1 \rightarrow {}^1E^a$ assignment is made in accordance with the methods and rationale of ref. 19.

19. R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967).

20. H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, New York, 1962.

21. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, 1970.

22. C. K. Jorgensen, *Acta Chem. Scand.*, **10**, 518 (1965); **11**, 151 (1957).

23. J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 6301 (1969).

24. Heating a sample of $[Ir(2\text{-phos})_2O_2]ClO_4$ at 150° for 24 h under vacuum will cause loss of O_2 and formation of $[Ir(2\text{-phos})_2]ClO_4$.

25. C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

26. See Chapter 3, page 115.

27. See Chapter 1, page 22.

28. a) R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970); b) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966).

29. a) J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, **94**, 4043 (1972); b) J. A. Labinger, A. V. Kramer, and J. A. Osborn, *J. Amer. Chem. Soc.*, **95**, 7908 (1973).

30. A. P. Ginsberg and W. E. Lindsell, *Chem. Commun.*, **1971**, 232.

31. A. P. Ginsberg, private communication.

CHAPTER III

Electronic Absorption and Emission Spectral Studies of Square Planar Rh(I) and Ir(I) Complexes

Introduction

Little previous effort has been devoted to the elucidation of the electronic structures and spectroscopic properties of low-spin $\underline{d}^8$ square planar complexes of Rh(I) and Ir(I). Only ambient temperature solution absorption spectra have been measured for complexes of the types $[MX(CO)L_2]$, $[M(2\text{-phos})_2]^+$, and $[M(2{=}\text{phos})_2]^+$ [1-5] (M = Rh(I), Ir(I); X = anionic or neutral ligand; L = monodentate, substituted phosphine or arsine; 2-phos is 1,2-bis(diphenylphosphino)ethane; 2=phos is cis-1,2-bis(diphenylphosphino)ethylene), and there have been no published reports at all of successful luminescence experiments.[6] Previous studies of the luminescence of low spin $\underline{d}^8$ square planar complexes have, in fact, been restricted to examples in which Pt(II) is the central metal,[8-11] and the broad and red-shifted emission bands in these Pt(II) species strongly suggest that the transitions originate in a highly distorted ligand field excited state.[12]

A systematic study of both the absorption and emission spectra of Rh(I) and Ir(I) complexes was thus initiated with the hope that detailed electronic structural information on the ground and lowest excited states will serve as a useful starting point in attempts to understand the rich oxidative addition chemistry of these species. These

Rh(I) and Ir(I) complexes generally show 3-4 bands in the visible-low energy uv spectral region, and previous interpretations of the spectra have led to the assignment of the bands as LF transitions.[1,3-5] This assignment has often been invoked in attempting to correlate the oxidative addition reactivity of a series of $IrX(CO)L_2$ complexes with the position of the lowest absorption band, and in general, the lower the band, the more reactive the complex.[1,14] The results reported herein, however, indicate that the low lying excited states in these complexes are not LF but metal to ligand charge transfer (MLCT) in nature.

This chapter is primarily concerned with the assignment of the lowest emission/absorption band systems in $[M(2\text{-phos})_2]^+$ and $[M(2{=}\text{phos})_2]^+$ complexes. However, the absorption and emission spectra of a few related complexes have also been measured, and these will be briefly discussed. Finally, the important conclusions from the study of the complexes with chelating phosphine ligands will be extended to the related $MX(CO)L_2$ systems.

Experimental Section

Preparation of Compounds. The chloride salts of $[M(2\text{-phos})_2]^+$ and $[M(2{=}\text{phos})_2]^+$ (M = Rh(I), Ir(I)) were prepared by the method of Vaska and Catone.[15] $[Rh(3\text{-phos})_2]Cl$, $[Rh(diars)_2]Cl$, and $[Rh(2\text{-ars})_2]Cl$ (3-phos is 1,2-bis(diphenylphosphino)propane; diars is 1,3-bis(dimethylarsino)benzene; 2-ars is 1,2-bis(diphenylarsino)ethane) were prepared in a similar manner. $IrCl(CO)(PPh_3)_2$ was purchased from Alfa

Chemical Corporation and was used without further purification. $\mathrm{RhCl(CO)(PPh_3)_2}$ was prepared by a published method,[16] the 2-phos and 2=phos ligands were obtained from Pressure Chemical Company, the 3-phos, diars, and 2-ars ligands were purchased from Strem Chemical Company, and $\mathrm{[Co(2{=}phos)_2]ClO_4}$ and $\mathrm{[Ni(2{=}phos)_2](ClO_4)_2}$ were gifts from Dr. Vince Miskowski. The perchlorate salts were prepared by addition of the chlorides to saturated solutions of $\mathrm{NaClO_4}$ in methanol. In all cases crystalline products were obtained. $\mathrm{[Pt(2\text{-}phos)_2](ClO_4)_2}$ and $\mathrm{[Pt(2{=}phos)_2](ClO_4)_2}$ were prepared by the procedure given by Westland.[17] Satisfactory elemental analyses were obtained for $\mathrm{[Rh(2\text{-}phos)_2]ClO_4}$ and $\mathrm{[Rh(2{=}phos)_2]ClO_4}$. *Anal.* Calcd for $\mathrm{[Rh(2\text{-}phos)_2]ClO_4}$: Rh, 10.31; P, 12.42; C, 62.50; H, 4.81. Found: Rh, 9.87; P, 12.39; C, 63.20; H, 4.53. Calcd for $\mathrm{[Rh(2{=}phos)_2]ClO_4}$: Rh, 10.35; P, 12.47; C, 62.75; H, 4.42. Found: Rh, 10.31; P, 11.84; C, 62.63; H, 4.93. The electronic absorption spectra of the oxygen-sensitive iridium complexes were found to be in excellent agreement with published data.[1]

Electronic Absorption Data. Electronic absorption spectra were measured using a Cary 17 spectrophotometer. Spectra at liquid nitrogen temperature were obtained using a low temperature dewar fitted with Suprasil quartz windows, and modified to hold a standard 1.00 cm cell. Measurements were performed in a 5:5:2 ethyl ether-isopentane-ethyl alcohol (EPA) solution and the low temperature spectra were corrected for solvent contraction. MCD spectra were obtained at the University of Southern California using a Cary 61 recording spectropolarimeter equipped with a Varian Associates superconducting magnet.

Emission and Excitation Data. Emission and excitation spectra were obtained using a Perkin-Elmer MPF-3A fluorescence spectrophotometer equipped with a standard accessory which corrects excitation spectra for varying lamp intensity and monochromator efficiency from 200 nm to 600 nm and corrects emission spectra for varying photomultiplier tube response and monochromator efficiency from 400 - 700 nm. All spectra reported in this paper are corrected. Measurements at 77 °K were performed using the standard low temperature phosphorescence attachment. Emission lifetimes were measured using a TRW decay time fluorometer equipped with a Xenon Corporation nanopulser excitation source. Emission intensity detected by an RCA 931A PMT, was displayed on a Tektronix 454 oscilloscope as a function of time. Plots of log (emission intensity) *vs.* time were linear in all cases. Emission quantum yields were measured relative to the standard $[Ru(bipyridine)_3]Cl_2$ ($\Phi = 0.376 \pm 0.036$).[18] Care was taken to match the optical density of the sample and the standard under the conditions of the measurement.

Results and Discussion

$[M(2\text{-phos})_2]Cl$ and $[M(2{=}phos)_2]Cl$ Complexes. Electronic spectral data for $[M(2\text{-phos})_2]Cl$ and $[M(2{=}phos)_2]Cl$ (M = Rh(I) and Ir(I)) are set out in Table III-1. Data for the analogous Pt(II) phosphine

Table III-1. Electronic Absorption Spectral Data for Some 2-phos and 2=phos Complexes

Complex	kcm^{-1} (ϵ_{max}), 300 °K	kcm^{-1} (ϵ_{max}), 77 °K
[Rh(2-phos)$_2$]Cl^a	21.3 (150)	21.3 (200)
	24.8 (5,150)	24.8 (9,250)
	31.8 (9,300)	31.6 (10,450)
	33.9 (8,400)	34.1 (11,570)
[Rh(2=phos)$_2$]Cl^a	21.1 (200)	20.7 (310)
	24.8 (4,900)	24.3 (12,700)
	29.4 (4,900)	28.4 (7,930)
		29.7 (8,100)
	32.3 (8,400)	31.3 (12,190)
[Ir(2-phos)$_2$]Cl^a	19.0 (800)	19.1 (1140)
	22.6 (5,300)	22.6 (8,700)
	26.2 (5,650)	26.3 (6,820)
	31.3 (13,100)	31.3 (14,690)
[Ir(2=phos)$_2$]Cl^a	19.0 (700)	18.6 (2,530)
	22.6 (3,900)	22.3 (11,410)
	26.5 (4,350)	26.0 (12,800)
		30.8 (15,300)
	32.1 (7,650)	32.0 (16,230)
[Pt(2-phos)$_2$](ClO$_4$)$_2$^{b}	32.6 sh (~ 3000)	--
	36.8 sh (30,000)	--
	29.5 (44,000)	--

Table III-1. (Continued)

Complex	kcm^{-1} (ϵ_{max}), 300 °K	kcm^{-1} (ϵ_{max}), 77 °K
[Pt(2=phos)$_2$]ClO$_4$)$_2$[b]	32.6 sh (3000)	--
	37.0 sh (24,000)	--
	42.9 (48,000)	--

---

[a] EPA solution.

[b] Ethanol solution.

complexes are given for comparison purposes. The room temperature and 77 °K absorption spectra of the four complexes are shown in Figures III-1 - III-4. It should be noted that the spectrum of $[Ir(2\text{-}phos)_2]Cl$ is similar to that of $[Ir(2{=}phos)_2]Cl$, except that the band at 31.3 kcm^{-1} is not resolved into two components upon cooling. $[Rh(2\text{-}phos)_2]Cl$ shows bands at 21.3 and 24.8 kcm^{-1}, similar to $[Rh(2{=}phos)_2]Cl$, but the pattern of bands at higher energy is significantly different.

Interpretation of the absorption spectra of both the $[M(2{=}phos)_2]^+$ and $[M(2\text{-}phos)_2]^+$ complexes is facilitated by assuming that the electronic transitions in question originate in a MP_4 core of D_{4h} symmetry. Square planar MP_4 core structures for $[Rh(2\text{-}phos)_2]^+$ and $[Ir(2\text{-}phos)_2]^+$ have been established by X-ray crystallographic studies of the perchlorate salts.[19] Vaska and coworkers have shown that the spectral, magnetic, and solution conductance properties of the $[M(2\text{-}phos)_2]Cl$ and $[M(2{=}phos)_2]Cl$ (M = Rh(I), Ir(I)) complexes are consistent with an analogous structural formulation.[1,15] In agreement with such a formulation, the electronic absorption and emission spectra of the perchlorate and respective chloride salts have been found to be virtually identical in both solids and in solution.

A simplified molecular orbital level scheme for a D_{4h} MP_4 core is shown in Figure III-5. The level ordering $b_{2g}(xy) < e_g(xz,yz) < a_{1g}(z^2) \ll a_{2u}\pi < b_{1g}(x^2 - y^2)$ is based on analogy to $Pt(CN)_4^{2-}$, which has been studied in considerable detail.[20,21] Ignoring spin-orbit

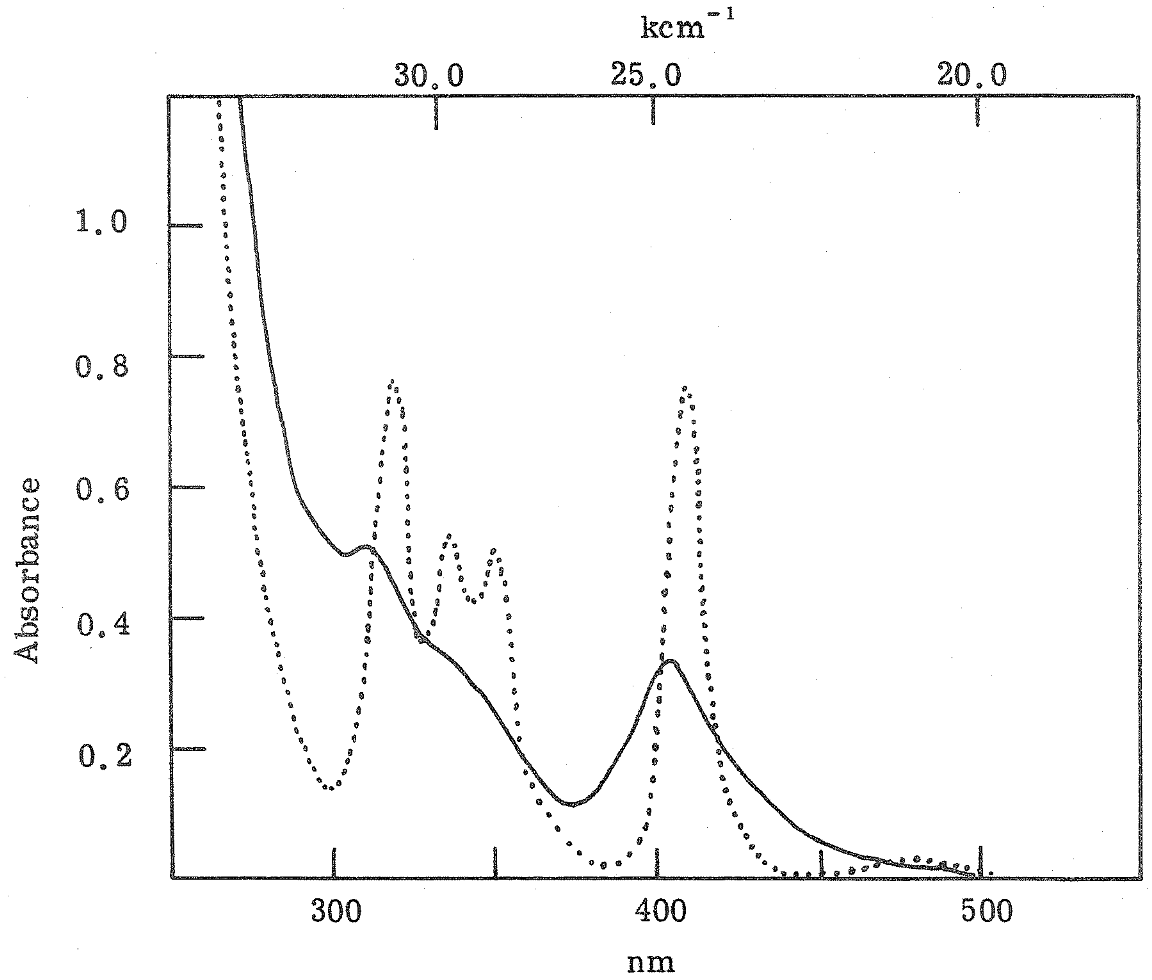


Figure III-1. Electronic spectra of $[\mathrm{Rh}(2\text{=phos})_2]\mathrm{Cl}$ in EPA solution at 300 °K (——) and 77 °K (----).

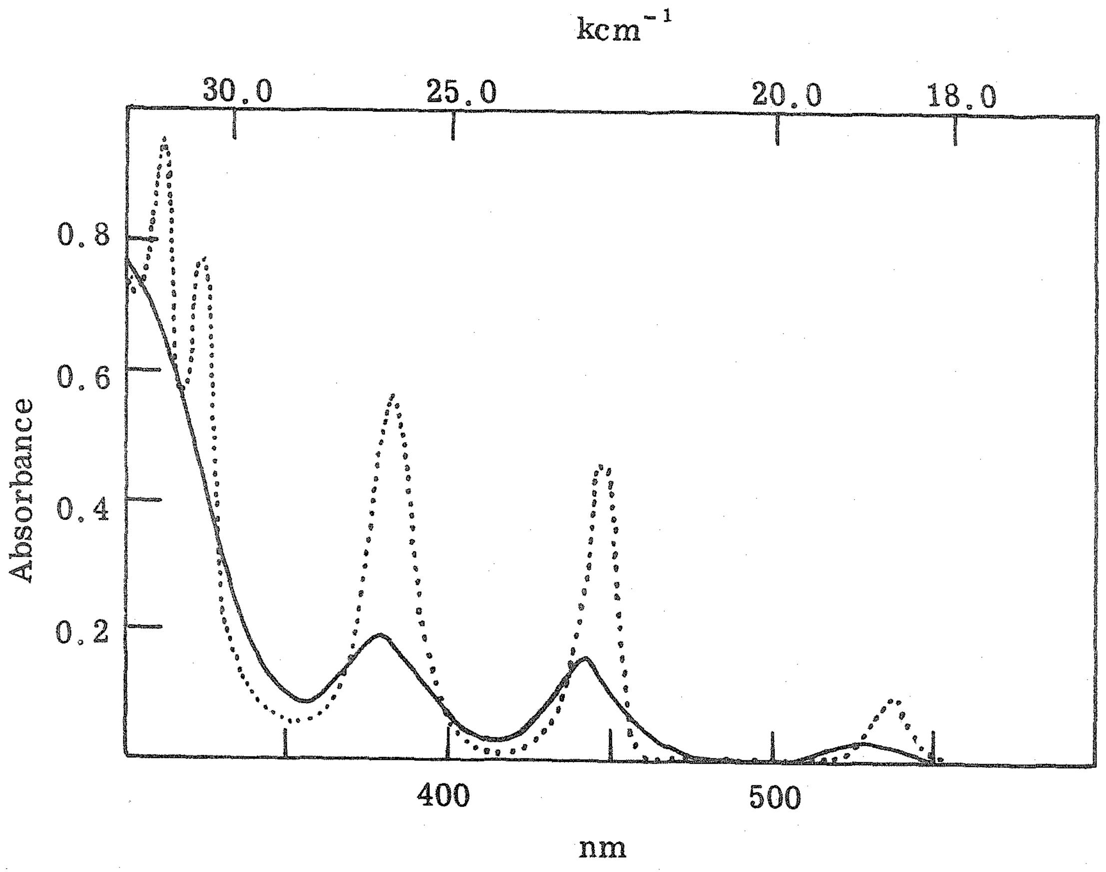


Figure III-2. Electronic Spectra of $[\mathrm{Ir}(2{=}\mathrm{phos})_2]\mathrm{Cl}$ in EPA solution at 300 °K (——) and 77 °K (····).

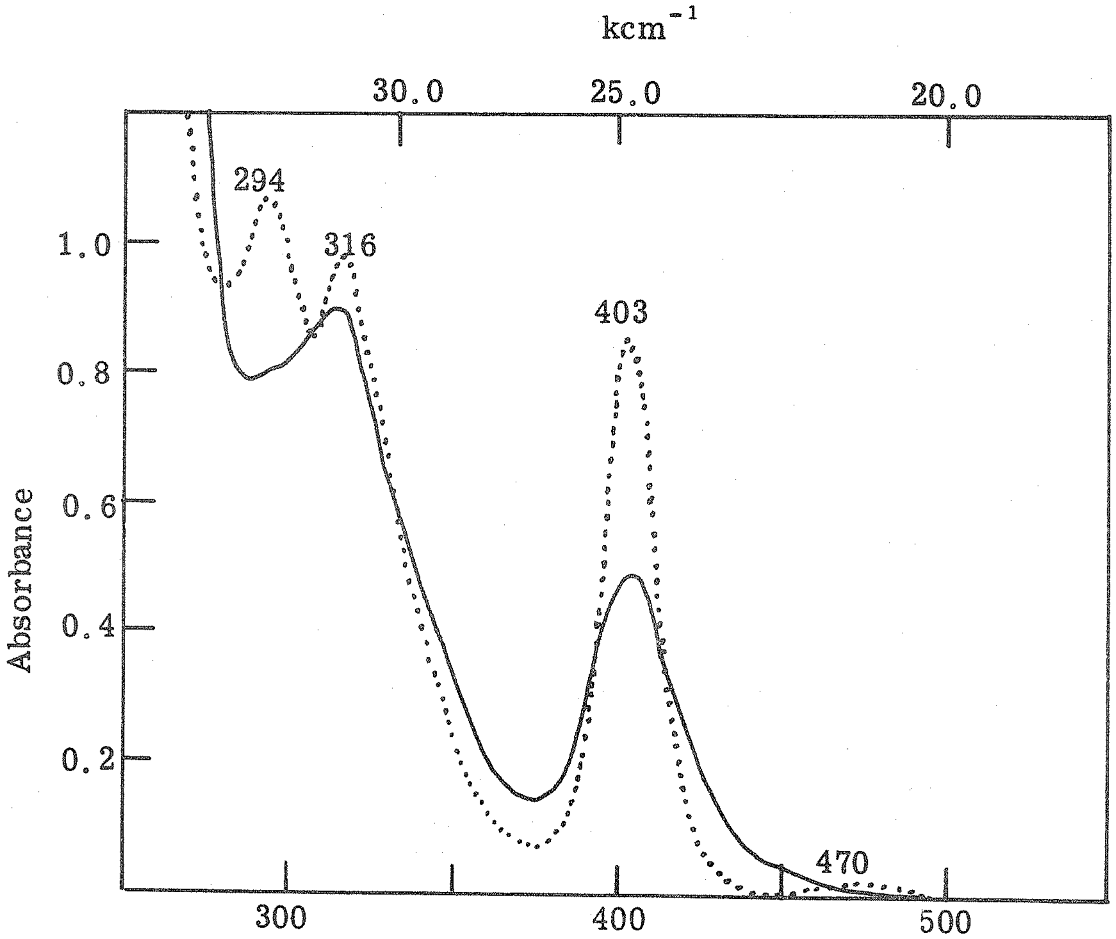


Figure III-3. Electronic spectra of [Rh(2-phos)$_2$]Cl in EPA solution at 300 °K (——) and 77 °K (····).

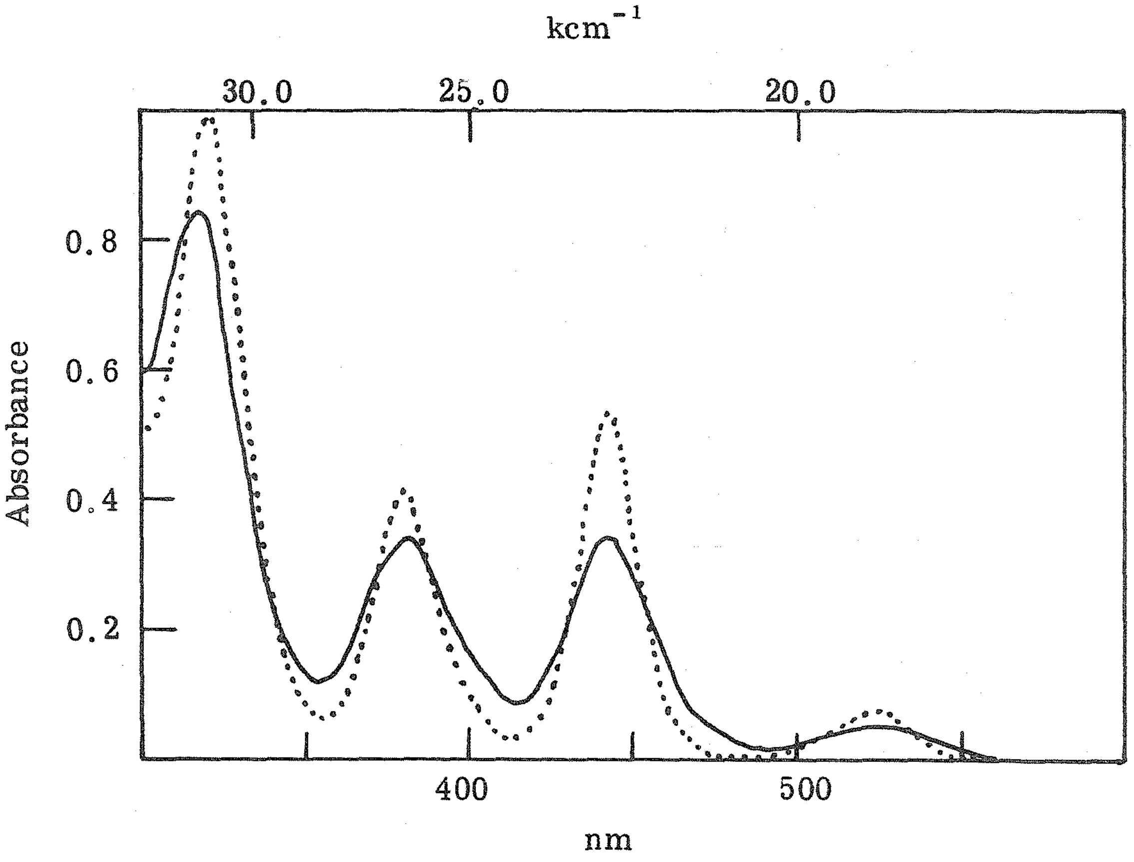


Figure III-4. Electronic spectra of [Ir(2-phos)$_2$]Cl in EPA solution at 300 °K (——) and 77 °K (····).

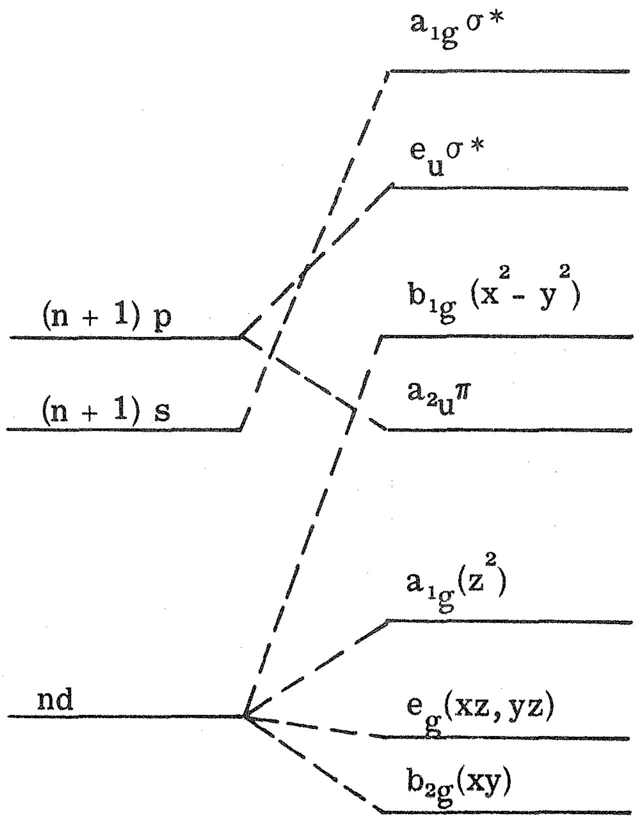


Figure III-5. Schematic molecular orbital energy level diagram for a square planar MP_4 complex.

coupling, three spin-allowed and three spin-forbidden LF transitions are expected to be associated with a ${}^1A_{1g}$ $(b_{2g}^2 e_g^4 a_{1g}^2)$ ground state system. In the series of square planar MP_4 complexes under investigation here, the energy ordering of the lowest LF transitions should be Rh(I) $\ll$ Ir(I) $\tilde{<}$ Pt(II). The other reasonable candidates for low energy excitation involve metal-to-ligand charge transfer (MLCT). These transitions, which originate in the metal d orbitals and terminate in the $a_{2u}\pi$ level, would be expected to occur in the energy order Ir(I) $<$ Rh(I) $\ll$ Pt(II).[22]

The large molar extinction coefficients of the absorption bands for the Rh(I) and Ir(I) complexes and the lack of any intensity decrease upon cooling to 77°K suggest that the bands are due to allowed charge transfer transitions. The absence of any bands below 32 kcm^{-1} in $[Pt(2\text{-phos})_2]^{2+}$ and $[Pt(2{=}phos)_2]^{2+}$ establishes the energy ordering Ir(I) $<$ Rh(I) $\ll$ Pt(II) and strongly supports an MLCT assignment. Further evidence for the MLCT interpretation may be derived from the the room temperature MCD spectra of $[Rh(2{=}phos)_2]Cl$ and $[Ir(2{=}phos)_2]Cl$ in CH_2Cl_2 solution, shown in Figures III-6 and III-7. Each spectrum clearly shows a positive A term for the lowest band and a B term for the next higher energy transition. This behavior is exactly analogous to that observed in the MCD spectrum of $Pt(CN)_4^{2-}$,[20] for which the two lowest bands have been interpreted[21] successfully in terms of the $d_{z^2} \rightarrow a_{2u}\pi$ transitions ${}^1A_{1g} \rightarrow E_u$ $({}^3A_{2u})$ and ${}^1A_{1g} \rightarrow A_{2u}$ $({}^1A_{2u})$, in order of increasing energy. On the basis of these results,

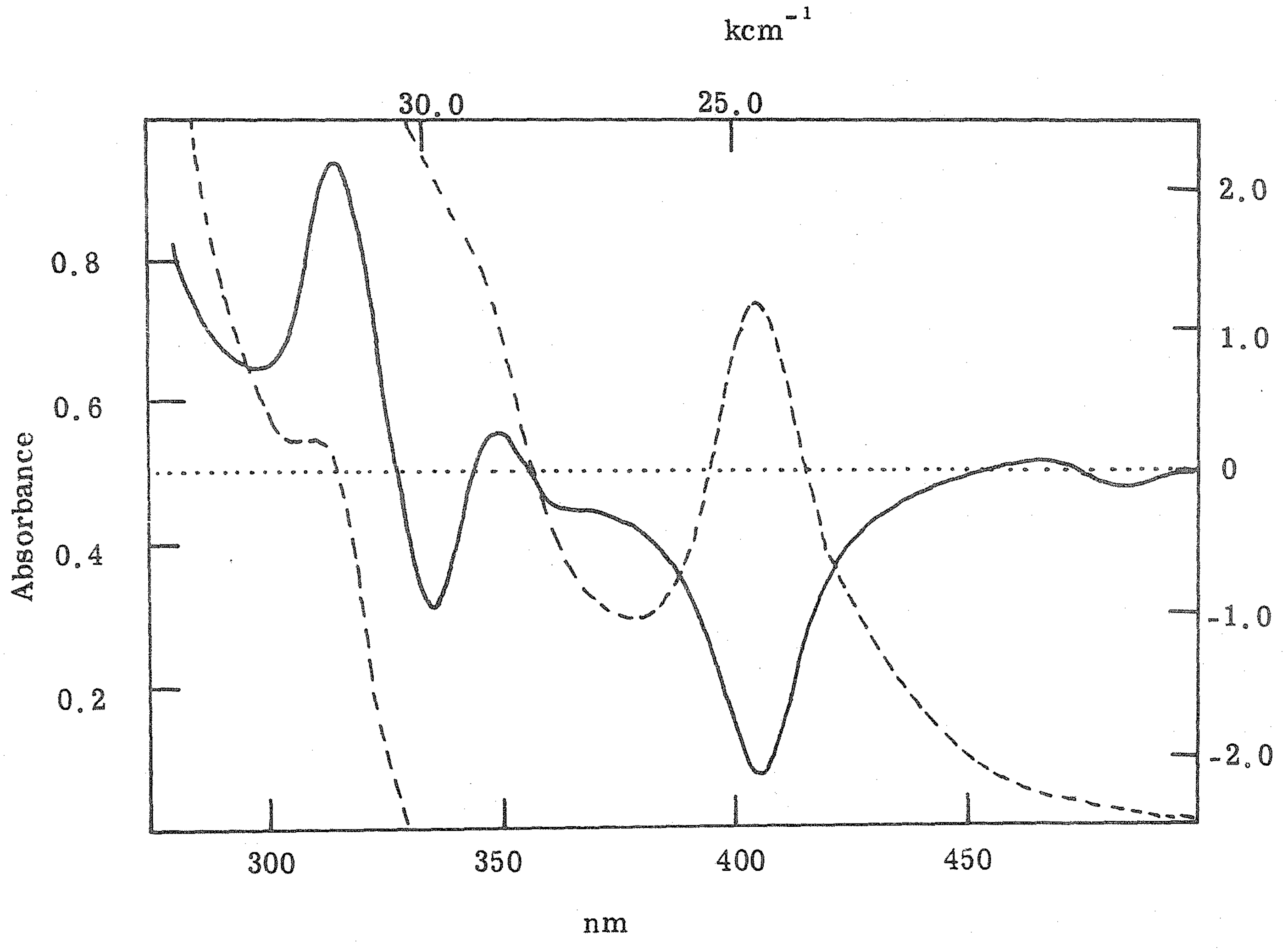


Figure III-6. Magnetic circular dichroism (——) and electronic absorption (---) spectra of [Rh(2=phos)$_2$] Cl in CH_2Cl_2 solution at 300°K.

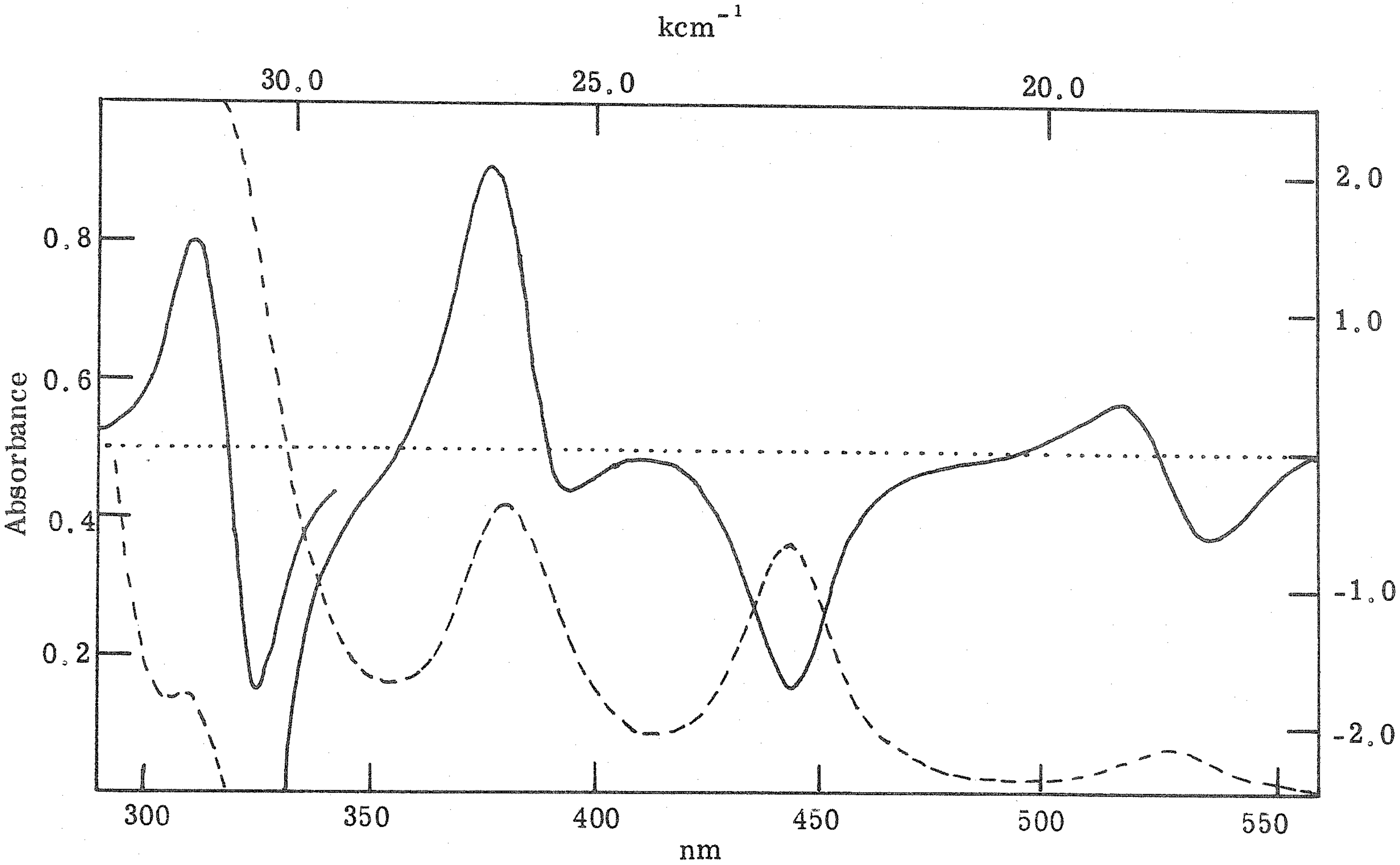


Figure III-7. Magnetic circular dichroism (——) and electronic absorption (---) spectra of [Ir(2=phos)$_2$] Cl in CH_2Cl_2 solution at 300°K.

the two lowest transitions in the Rh(I) and Ir(I) complexes are assigned analogously.

Electronic emission data for [M(2=phos)$_2$]Cl and [M(2-phos)$_2$]Cl (M = Rh(I), Ir(I)) are set out in Table III-2. The absorption, emission, and excitation spectra of [Ir(2=phos)$_2$]Cl in EPA at 77°K are shown in Figure III-8. Figure III-9 illustrates the degree of overlap of the 77°K absorption and emission spectra of the complexes. All but [Rh(2-phos)$_2$]Cl emit very intensely in the solid state at room temperature, although none of the complexes was found to luminesce in degassed ethanol solution. The solid state emission intensity increases considerably on cooling and a bright-orange luminescence is observed for [Rh(2-phos)$_2$]Cl at 77°K. All four complexes emit when dissolved in an EPA glass at 77°K, and the excitation spectrum of each complex was found to correspond to the low temperature absorption spectrum, establishing that internal conversion from the upper excited states to the luminescent state is efficient.

Particularly striking is the unusually sharp, strongly overlapping emission/absorption system of [Ir(2=phos)$_2$]Cl (Figure III-8). The large emission quantum yield (0.93 ± 0.07) for this complex is also noteworthy. The observed degree of overlap and the similar widths of the absorption and emission bands of [Ir(2=phos)$_2$]Cl establish that the emitting state possesses an undistorted square planar structure. These results are entirely consistent with a $\underline{d}^7 a_{2u}$ excited state as the emitting level. The a_{2u} MO is π bonding between the metal p_z valence orbital

Table III-2. Electronic Emission Data for Some Rhodium(I) and Iridium(I) Bis-diphosphine Complexes in EPA at 77°K

Complex	Maximum kcm^{-1}	Emission Halfwidth cm^{-1}	Quantum Yield	Emission Lifetime, μsec
[Rh(2-phos)$_2$]Cl	16.3	2120	0.052 ± 0.005	20.8
[Rh(2=phos)$_2$]Cl	17.1	2890	0.75 ± 0.07	27.5
	(16.5)[a]	(2880)[a]		(22.3)[a]
[Ir(2-phos)$_2$]Cl	17.1	1610	0.25 ± 0.03	9.8
	(17.7)[a]	(1480)		(0.4 ± 0.2)[a]
[Ir(2=phos)$_2$]Cl	18.4	340	0.93 ± 0.07	8.2
	(18.1)[a]	(1720)[a]		(1.4 ± 0.2)[a]

[a] Solid sample at room temperature.

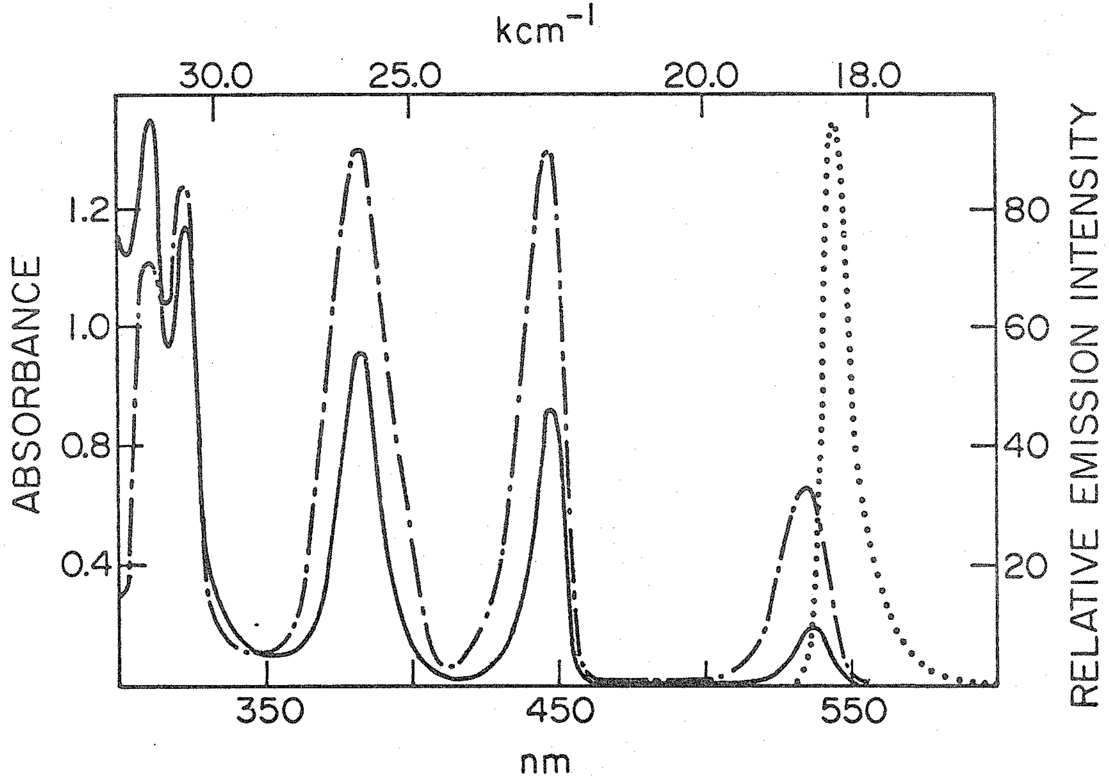


Figure III-8. Electronic absorption (——), excitation (·-·-·-), and emission (···) spectra of [Ir(2=phos)$_2$]Cl in EPA solution at 77°K.

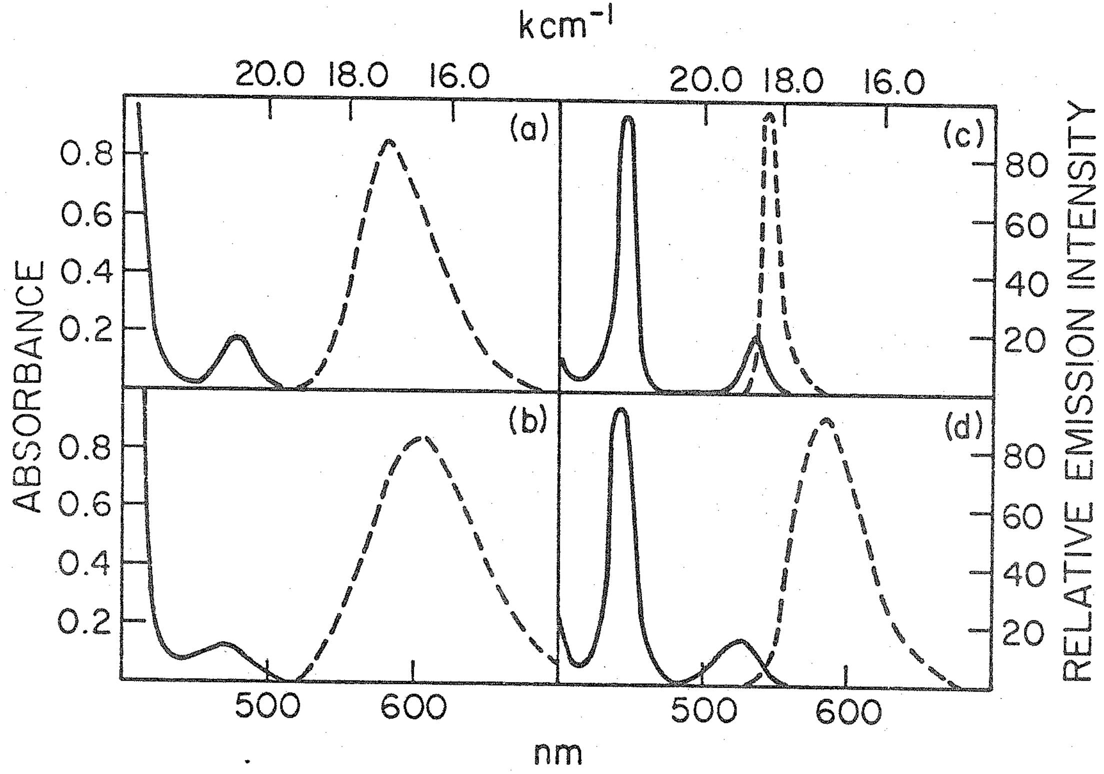


Figure III-9. Electronic absorption (——) and emission (- - -) spectra of (a) [Rh(2=phos)$_2$]Cl, (b) [Rh(2-phos)$_2$]Cl, (c) [Ir(2=phos)$_2$]Cl, and (d) [Ir(2-phos)$_2$]Cl in EPA at 77°K.

and appropriate 3$\underline{d}\pi$ orbitals of the four phosphorus donor atoms and should be rigorously square planar. Thus it is highly probable that an E_u ($^3A_{2u}$) excited state is involved in the emission/absorption system. It may also be noted that the observed emission lifetime (Table III-2) is consistent with the substantial degree of spin-forbidden character of the transition E_u ($^3A_{2u}$) $\rightarrow$ $^1A_{1g}$.

Although evidence indicates that the absorption bands are also primarily of the type $\underline{d} \rightarrow a_{2u}$, the emission spectra of $[Rh(2\text{-phos})_2]^+$, $[Rh(2{=}phos)_2]^+$, and $[Ir(2\text{-phos})_2]^+$ are significantly broader than that of $[Ir(2{=}phos)_2]^+$. Of greater concern, however, is the observation that the emission maxima of the rhodium complexes are red-shifted by about 4000 cm^{-1} from the lowest absorption peaks (Figure III-9). The observed red shifts and half-widths associated with the emission bands of the Rh(I) complexes imply that the MP_4 cores in the emitting states are somewhat distorted from the ground state D_{4h} geometry. Such an effect could signal that the emitting state is not purely MLCT in character, but possesses a small admixture of one or more of the LF states which have their potential energy minima on a D_{2d} (distorted tetrahedral) surface.[13] Such MLCT-LF mixing should be much more important in the rhodium complexes than for their iridium counterparts, as the LF states are expected to be much lower in energy (and therefore in closer proximity to the MLCT states) in the former case.

[Rh(3-phos)$_2$]Cl, [Rh(2-ars)$_2$]Cl, and [Rh(diars)$_2$]Cl. Electronic spectral data for these complexes are set out in Table III-3 and emission and excitation spectra in EPA solution at 77°K are shown in Figures III-10 - III-12. Although these spectra were not analyzed in as great a detail as those of [Rh(2-phos)$_2$]$^+$ and [Rh(2=phos)$_2$]$^+$, certain conclusions can be drawn concerning them. The electronic absorption spectra of these Rh(I) complexes are quite similar to the 2-phos and 2=phos analogs, each showing a low intensity band around 20.0 - 22.0 kcm^{-1} and a more intense band around 23.0 - 25.0 kcm^{-1}. By analogy, the low intensity band can be assigned as $^1A_{1g} \rightarrow E_u\ (^3A_{2u})$ and the higher energy transition is $^1A_{1g} \rightarrow A_{2u}\ (^1A_{2u})$. It is interesting to note that the absorption maxima of [Rh(2-ars)$_2$]$^+$ are at slightly lower energies than in any of the other Rh(I) species.

These complexes have been observed to luminesce in the solid state and in EPA solution at 77°K. However, the observed emission is quite weak in each case and appears to be at least an order of magnitude less intense than the emission from [Rh(2-phos)$_2$]$^+$. An examination of the spectra in Figures III-10 - III-12 shows that the emission is quite broad and is substantially red-shifted from the lowest absorption peak. Again, such properties can be attributed to an admixture of one or more of the LF states into the luminescent state, and in the case of [Rh(3-phos)$_2$]$^+$ to a greater flexibility of the ligand backbone, giving rise to more efficient radiationless decay paths.

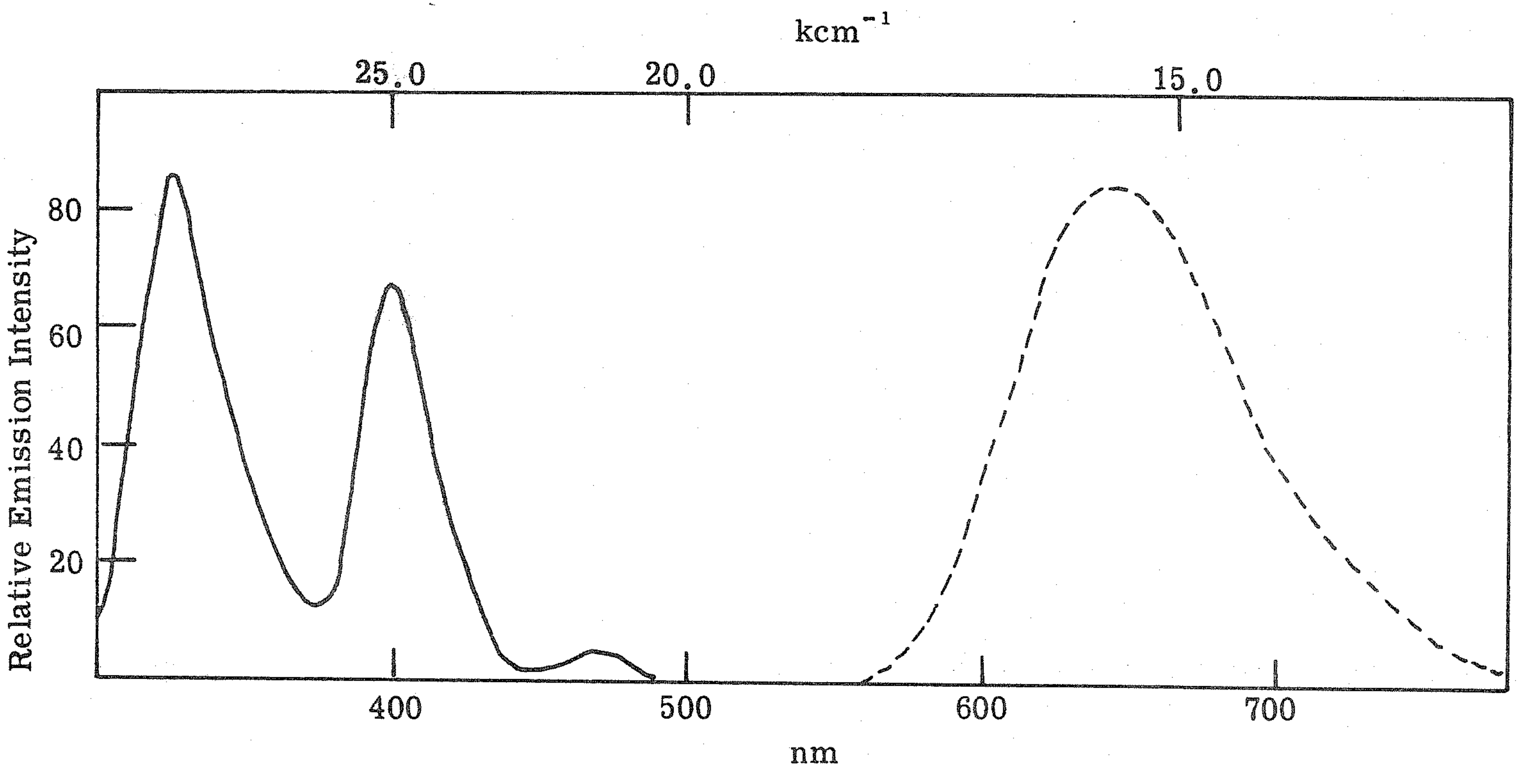


Figure III-10. Excitation (——) and emission (- - -) spectra of $[Rh(3\text{-}phos)_2]Cl$ in EPA solution at 77 °K.

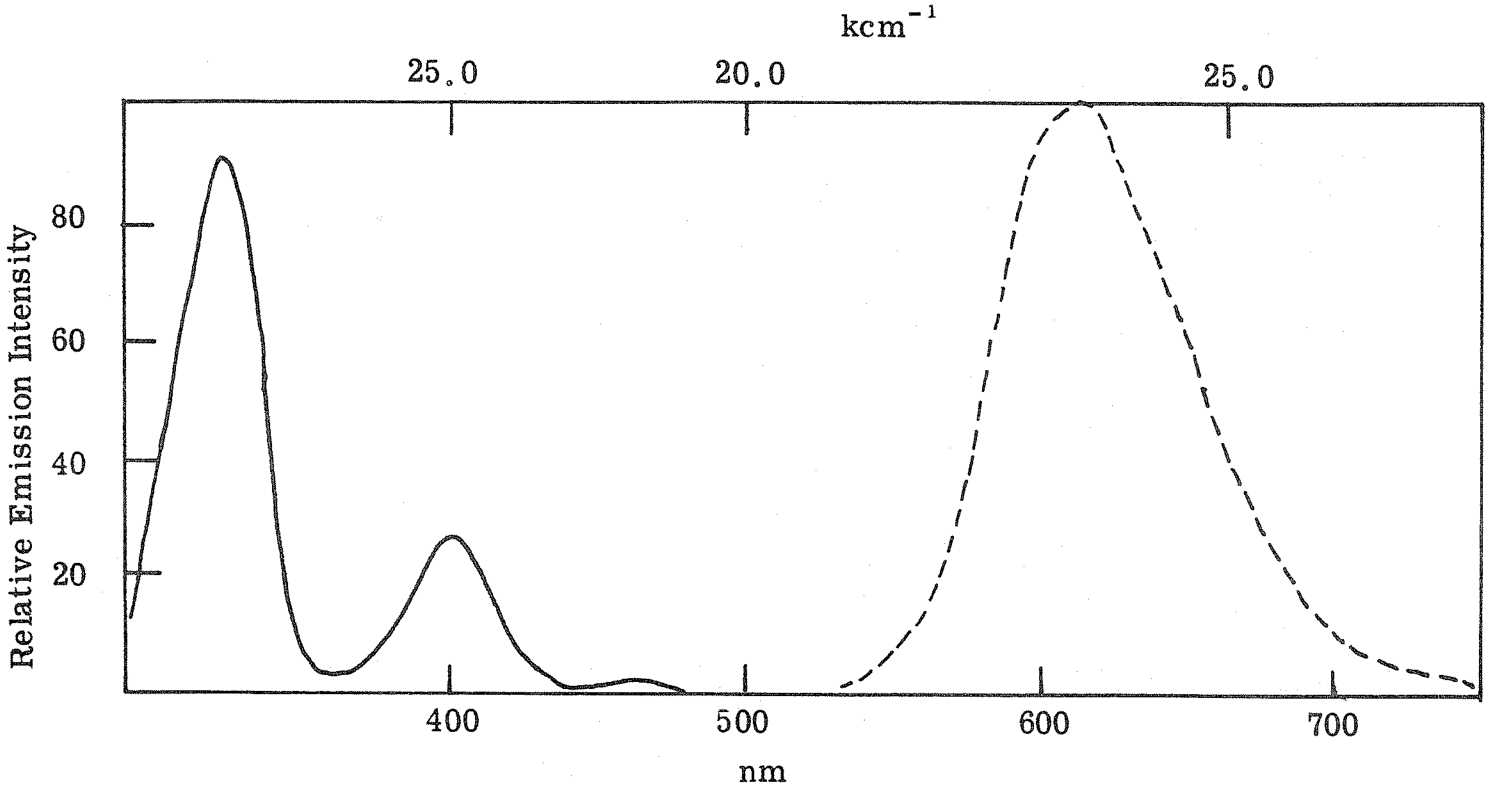


Figure III-11. Excitation (——) and emission (- - -) spectra of [Rh(diars)$_2$] Cl in EPA solution at 300 °K.

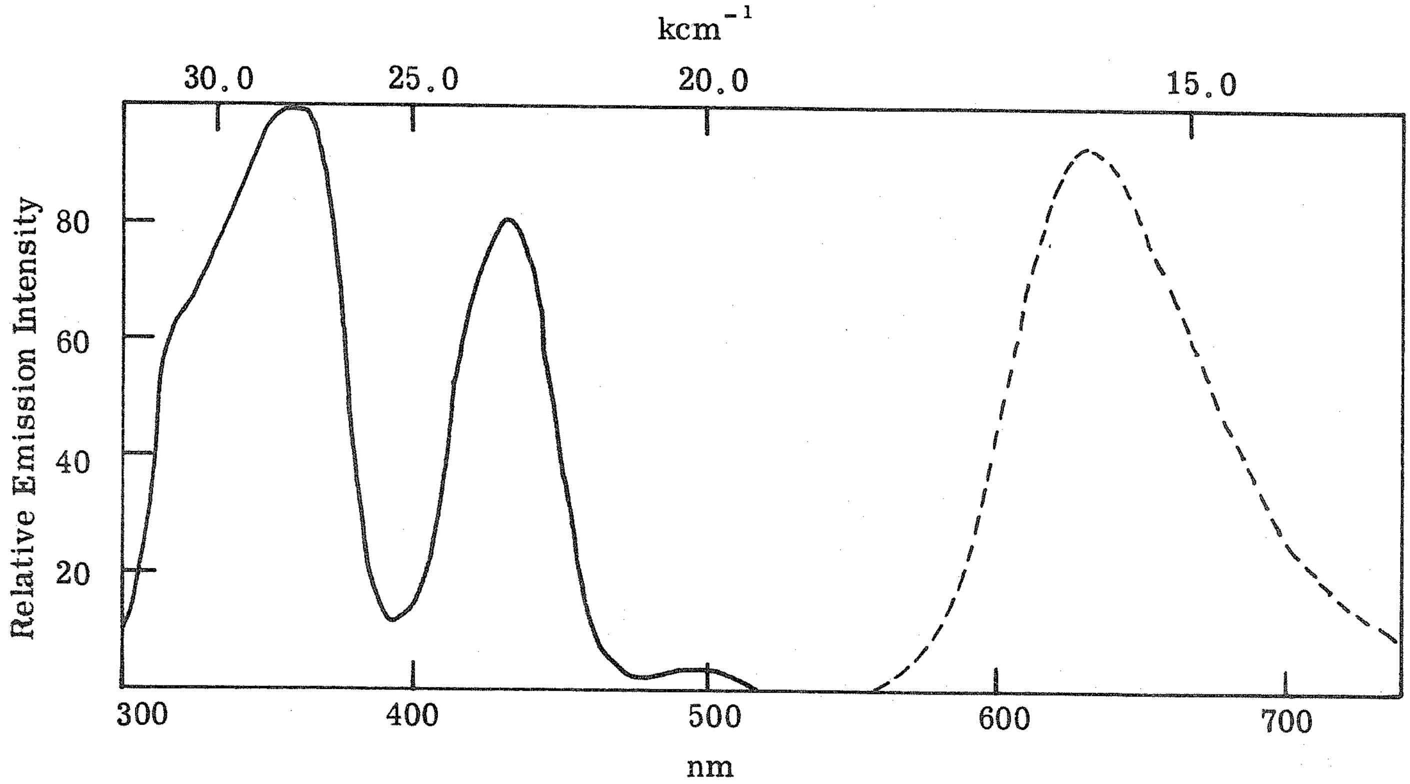


Figure III-12. Excitation (——)and emission (---) spectra of [Rh(2-ars)$_2$] Cl in EPA solution at 77°K.

Table III-3. Electronic Absorption Spectral Data for Some Rh(I) Complexes in EPA at 77°K

Complex	Absorption Maxima kcm^{-1}
$[Rh(3\text{-}phos)_2]Cl$	21.4
	25.0
$[Rh(diars)_2]Cl$	21.5
	25.1
$[Rh(2\text{-}ars)_2]Cl$	20.2
	23.1

Non-luminescent Complexes. The following complexes were prepared and were found to be non-luminescent:

$IrCl(CO)(PPh_3)_2$
$IrI(CO)(PPh_3)_2$
$IrSCN(CO)(PPh_3)_2$
$RhCl(CO)(PPh_3)_2$
$[Co(2{=}phos)_2O_2]BF_4$
$[Co(2{=}phos)_2Br_2]Br$
$[Ir(2{=}phos)_2O_2]Cl$
$[Ir(2\text{-}phos)_2O_2]Cl$
$[Ni(2{=}phos)_2](ClO_4)_2$
$[Co(2{=}phos)_2]ClO_4$

There is still some uncertainty as to whether $[Co(2{=}phos)_2]ClO_4$ is luminescent or not. Although no emission was detected with our instrumental set-up, it is conceivable that emission occurs beyond the limits of our detection ability (12.5 kcm^{-1}), especially since the lowest absorption band is at 13.89 kcm^{-1}.[23] A very weak blue luminescence was observed from $[Pt(2\text{-}phos)_2]^{2+}$ and $[Pt(2{=}phos)_2]^{2+}$ in EPA solution at 77°K.[24] However, these complexes are quite insoluble and it was never determined whether the observed emission was from the complexes or from some organic impurity.

Summary

A very important aspect of this study is the assignment of the bands in the absorption spectra of these square-planar complexes as metal-to-ligand charge transfer rather than ligand field. The previous assumption of LF transitions has often been invoked in attempting to explain the oxidative addition reactivity of a series of $MX(CO)L_2$ (M = Rh(I), Ir(I)) complexes, as X varies through a wide variety of anionic or neutral ligands and the nature of the phosphine or arsine L is varied.[1,14] Electronic spectral data for some of these complexes are set out in Tables III-4 and III-5.[2-4,25] It can be seen that the spectra are quite similar to those of $[M(2{=}phos)_2]^+$ and $[M(2\text{-}phos)_2]^+$, and it is quite probable that the bands are also due to MLCT transitions, rather than the previous interpretations of LF transitions.

In the luminescent complexes described herein, and especially those of Ir(I), the transition in emission is essentially from a metal-ligand bonding molecular orbital ($a_{2u}\pi$) to a metal-ligand nonbonding orbital (d_{z^2}). This highly unusual type of luminescence, giving rise to a very high quantum yield and a very narrow emission band (in the case of $[Ir(2{=}phos)_2]^+$), should spark considerable investigations into properties of related complexes and attempts to find other complexes with similar properties. The high absorbance throughout the visible region, the emission centered at 18.4 kcm^{-1}, near the region of the maximum of eye sensitivity, and the very high quantum yield of $[Ir(2{=}phos)_2]^+$ suggest that the compound has a potential use as the luminescing agent in a screen or a film. The compound has been placed in a polymethylmethacrylate film and the emission properties have been observed to persist. Unfortunately, $[Ir(2{=}phos)_2]^+$ is oxygen

Table III-4. Electronic Absorption Spectral Data for Some $IrX(CO)L_2$ Complexes

Complex	Absorption Maxima kcm^{-1} (ϵ_{max})	Reference
$IrCl(CO)(PPh_3)_2$	22.7 (438)	2
	25.8 (3,523)	
	29.6 (2,183)	
$IrBr(CO)(PPh_3)_2$	22.5 (270)	2
	25.6 (3,828)	
	29.8 (1,865)	
$IrI(CO)(PPh_3)_2$	22.2 (704)	2
	25.2 (3,109)	
	28.1 (3,139)	
$IrCl(CO)[P(C_6H_{11})_3]_2$	23.1 (632)	2
	26.3 (3,378)	
	29.7 (2.389)	
$IrCl(CO)[P(i\text{-}C_3H_7)_3]_2$	23.1 (616)	2
	26.4 (3,261)	
	29.8 (2,414)	
$IrF(CO)(PPh_3)_2$	23.4 (815)	3
	26.5 (4,300)	
	29.9 (3,740)	

Table III-4. Continued

Complex	Absorption Maxima kcm^{-1} (ϵ_{max})	Reference
$IrN_3(CO)(PPh_3)_2$	22.6 (744)	3
	25.5 (3, 600)	
	28.8 (3, 200)	
$IrCN(CO)(PPh_3)_2$	20.4 (470)	3
	23.7 (3, 470)	
	27.3 (3, 620)	

Table III-5. Electronic Absorption Spectral Data for Some $RhX(CO)L_2$ Complexes

Complex	Absorption Maxima kcm^{-1} (ϵ_{max})	Reference
$Rh(ClO_4)(CO)(PPh_3)_2$	28.6 (3160)	3
$RhF(CO)(PPh_3)_2$	27.9 (4000)	3
$RhN_3(CO)(PPh_3)_2$	27.4 (4220)	3
$RhBr(CO)(PPh_3)_2$	27.1 (3680)	3
$RhCN(CO)(PPh_3)_2$	24.9 (4270)	3

sensitive and in such a film it slowly (3-4 days) adds oxygen to give the non-luminescent oxygen adduct.

References

1. L. Vaska, L. S. Chen, and W. V. Miller, J. Amer. Chem. Soc., 93, 6671 (1971).
2. W. Strohmeier and F. J. Müller, Z. Naturforsch., B24, 770 (1969).
3. J. Peone, Jr., Ph.D. Dissertation, Clarkson College of Technology, Potsdam, New York, 1971.
4. L. S. Chen, Ph.D. Dissertation, Clarkson College of Technology, Potsdam, New York, 1971.
5. F. A. Taylor in "Homogeneous Catalysis," ACS Adv. Chem. Ser. No. 70, American Chemical Society Publications, Washington, D.C., p. 201.
6. L. Vaska and R. Brady have independently observed luminescence from several Rh(I) and Ir(I) complexes containing phosphine and arsine ligands. Their work will be described elsewhere.[7]
7. L. Vaska, private communication.
8. P. D. Fleischauer and P. Fleischauer, Chem. Rev., 70, 199 (1970); and references therein.
9. P. Natarajan and A. W. Adamson, J. Amer. Chem. Soc., 93, 5599 (1971).
10. D. L. Webb and L. A. Rossiello, Inorg. Chem., 9, 2622 (1970); ibid., 10, 2213 (1971).
11. H. H. Patterson, J. J. Godfrey, and S. M. Kahn, Inorg. Chem., 11, 2872 (1972).

12. Convincing theoretical arguments have been presented to the effect that the ligand field B_{1g} and E_g states are unstable with respect to distortion to the tetrahedral D_{2d} states B_1 and E, respectively. Interestingly, the A_{2g} states should be stable in D_{4h} symmetry.[13]

13. C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks, and C. R. Hare, *Inorg. Chem.*, **4**, 514 (1965).

14. M. Kubota, G. W. Kiefer, R. M. Ishikawa, and K. E. Bencala, *Inorg. Chim. Acta*, **7**, 195 (1973).

15. L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, **88**, 5324 (1966).

16. D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Syn.*, **11**, 99 (1968).

17. A. D. Westland, *J. Chem. Soc.*, 3060 (1965).

18. J. N. Demas and G. A. Crosby, *J. Amer. Chem. Soc.*, **93**, 2841 (1971).

19. M. C. Hall, B. T. Kilbourn, and K. A. Taylor, *J. Chem. Soc. A*, 2539 (1970).

20. S. B. Piepho, P. N. Schatz, and A. J. McCafferty, *J. Amer. Soc.*, **91**, 5994 (1969).

21. C. D. Cowman and H. B. Gray, to be submitted for publication.

22. a) H. B. Gray, *Transition Metal Chem.*, **1**, 239 (1965);
b) C. J. Ballhausen and H. B. Gray in "Coordination Chemistry," A. E. Martell, Ed., Vol. 1, Van Nostrand Reinhold Co., New York, 1971.

23. C. F. Nobile, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, **5**, 698 (1971).

24. M. Keil, private communication.

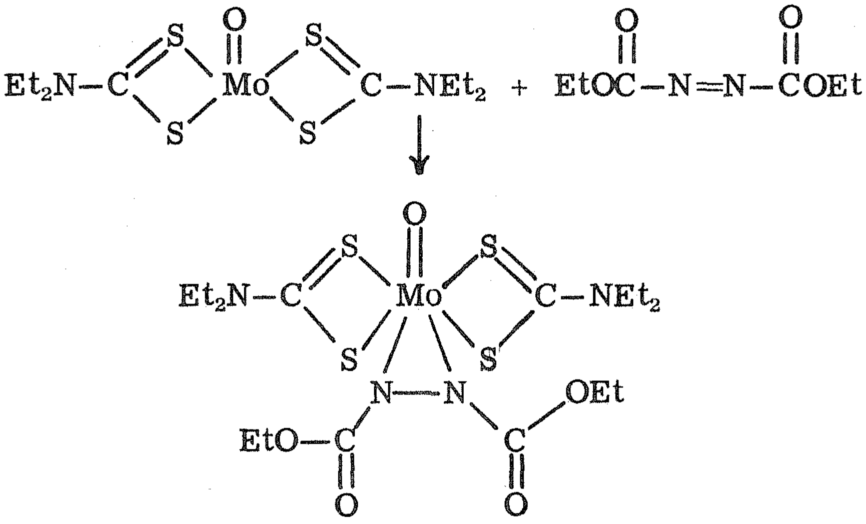
25. L. Vaska, private communication.

CHAPTER IV

An Investigation into the Photochemical Properties of Quadruply Bonded Metal-Metal Dimers

Introduction

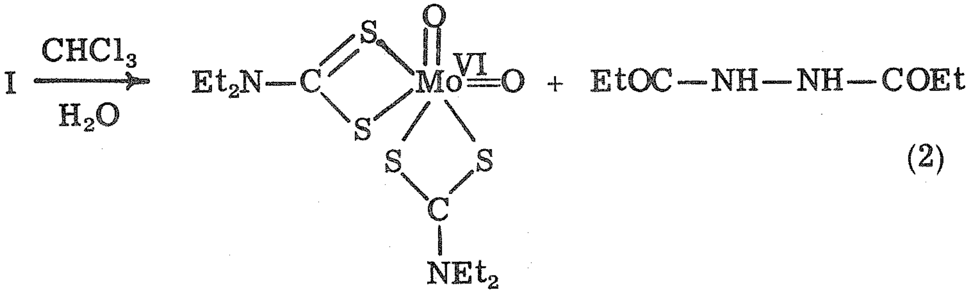
This chapter is a report of an investigation into the photochemical properties of quadruply bonded metal-metal dimers. Interest arose in these dimers as a result of a 1972 report by Schneider and coworkers. They observed oxidative-addition of diethylazodicarboxylate to oxo-bis(N,N-diethyldithiocarbamato)-molybdenum(IV), giving a seven coordinate Mo(VI) complex (Eq. 1):[1]



(1)

I

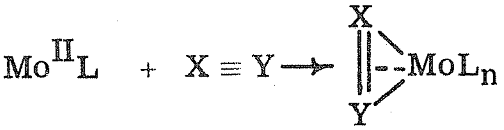
When moist chloroform is added to a solution of I, it is hydrolyzed to a Mo(VI) dioxo complex and 1,2-bis(ethoxycarbonyl)hydrazine, thus affecting reduction of the nitrogen-nitrogen double bond to a nitrogen-nitrogen single bond (Eq. 2)[1]:



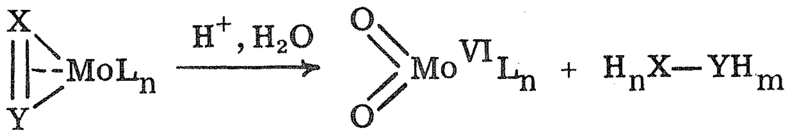
(2)

This reaction proceeds partly because Mo(IV), with a $\underline{d}^2$ electron configuration, is not a particularly stable oxidation state of molybdenum. Molybdenum would prefer to be in the more stable $\underline{d}^0$-Mo(VI) state, and in the two electron process shown above, Mo(IV) goes to Mo(VI). Mo(II), with a $\underline{d}^4$ configuration, is even less stable than Mo(IV), and is expected to readily undergo a 4 electron oxidation to give Mo(VI).

The original goal of this study was to generate a reactive Mo(II) complex and hopefully observe a <u>four electron transfer</u> to some unsaturated substrate ($X \equiv Y$) to give Mo(VI) and a reduced substrate (Eqs. 3 and 4):



(3)



(4)

Possible substrates for this type of four electron process include substituted acetylenes, nitriles, isonitriles, and possibly molecular nitrogen. This type of reaction has not been demonstrated before, quite possibly because of the relative scarcity of Mo(II) complexes. The few that are known are quadruply bonded metal-metal dimers, metal cluster compounds, and monomeric species containing carbonyl, phosphine, or arsine ligands.[2] These ligands tend to stabilize the low oxidation state and prevent the four electron oxidation from occurring. The goal of this study was then to try to generate a reactive, monomeric Mo(II) complex photochemically.

Irradiation of single metal-metal bonded dimers has been shown to lead to cleavage of the metal-metal bond.[3,4] In dirhenium dodecacarbonyl and dimanganese dodecacarbonyl, the lowest bands in the absorption spectra have been assigned as $d\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$.[5] Irradiation into this band system has been shown to lead to cleavage of the metal-metal bond and generation of reactive $\underline{d}^7$ fragments (Eq. 5):

$$(CO)_5Re^0\!-\!Re^0(CO)_5 \xrightarrow{hv} 2Re^0(CO)_5 \qquad (5)$$

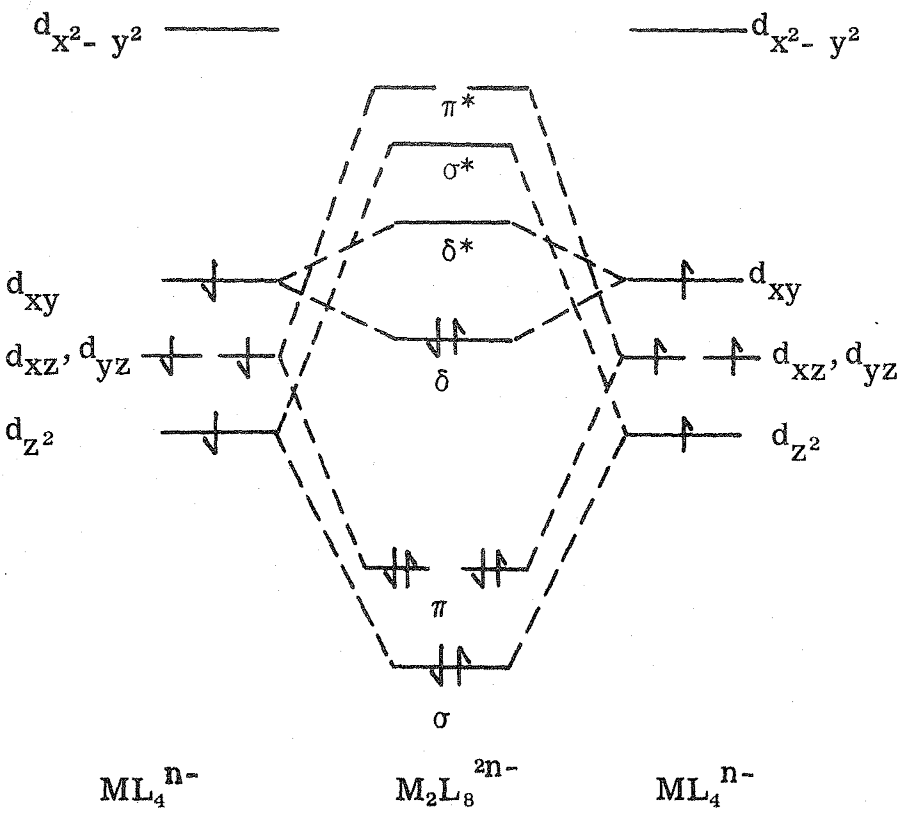
These fragments either dimerize to regenerate the starting material or react with added ligand or solvent to give stable $\underline{d}^6$ 6-coordinate species (Eq. 6)[4]:

$$Re^0(CO)_5 + CCl_4 \longrightarrow ClRe^I(CO)_5 + \cdot CCl_3 \qquad (6)$$

If it is possible to irradiate single metal-metal bonded dimers, cleave the metal-metal bond, and generate reactive fragments, then it could be possible to irradiate quadruply bonded metal-metal dimers, cleave the quadruple bond, and generate extremely reactive fragments. For example, photolysis of quadruply bonded Mo(II) dimers could generate the reactive monomeric Mo(II) complexes sought for the four electron process described earlier (Eq. 7):

$$Mo_2^{II}L_{2n} \xrightarrow{h\nu} 2Mo^{II}L_n \xrightarrow{\text{4-electron process}} \qquad (7)$$

Essentially all the pioneering work in investigating the reactions and structures of quadruply bonded metal-metal dimers has been performed by F. Albert Cotton and his coworkers.[6] To date, three metals have been demonstrated to form such dimers: molybdenum(II), rhenium(III), and technetium(III).[6] The model compound and the one that has been most investigated is $Re_2Cl_8^{2-}$. The crystal structure of this compound shows a very short metal-metal distance, 2.24Å compared to 2.75Å in the metal, and shows that the chlorides are in the eclipsed rotational configuration.[7] In order to explain these two phenomena, a quadruple bond was proposed, and the molecular orbital scheme shown in Figure IV-1 was devised.[8] The quadruple bond consists of a σ bond formed by overlap of the d_{z^2} orbitals, 2 π bonds formed by overlap of the d_{xz}, d_{yz} orbitals, and a δ bond formed by overlap of the d_{xy} orbitals. In addition to the bonding and the anti-bonding orbitals shown in Figure IV-1, there are two non-bonding σ_N orbitals localized mainly on the axis of the molecule, pointing away from the metal-metal bond. These orbitals arise as a result of mixing of the metal d_{z^2} orbitals and the higher energy metal p_z



M = Mo(II), Re(III)

Figure IV-1. Molecular orbital diagram for a quadruply bonded metal-metal dimer.

orbitals.[8] In the ground state of the molecule, these σ_N orbitals are empty and the electronic configuration is $\sigma^2\pi^4\delta^2$.

The exact position of the σ_N bonding orbital has been much discussed.[8-12] Cotton originally proposed the energy level ordering $\delta < \sigma_N < \delta^*$ based primarily upon his analysis of the electronic absorption spectrum of $Re_2Cl_8^{2-}$, shown in Figure IV-2.[8,9] He assigned the band at 14.7 kcm^{-1} as $\delta \rightarrow \sigma_N$, arguing that the observed oscillator strength of the band is too low for the allowed $\delta \rightarrow \delta^*$ transition.[8] This assignment was further supported by an extended Hückel molecular orbital calculation which gave the same energy level ordering and an estimate of the quadruple bond energy of $Re_2Cl_8^{2-}$ as 366 kcal/mole.[9] Many workers have since assumed that these quadruple bonds are the strongest bonds known in chemistry.[6]

Recently Gray and Cowman measured the polarized electronic absorption spectrum of a single crystal of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ at 5 °K and provided very convincing evidence that the band at 14.7 kcm^{-1} is not a $\delta \rightarrow \sigma_N$ transition but is rather the $\delta \rightarrow \delta^*$ transition.[12,13] Furthermore, the weak bands at 27.0 and 28.3 kcm^{-1} were assigned as $\sigma \rightarrow \delta^*$ and $\delta \rightarrow \sigma_N$.[13] The fact that the $\delta \rightarrow \delta^*$ transition is at lower energy than previously thought by Cotton casts some doubt on his estimate of the quadruple bond energy.

Despite the very large estimate of the bond energy, an investigation into the photochemical properties of these quadruply bonded dimers was initiated with the hope of observing interesting chemistry. At the start of this study, several Re(III) dimers were

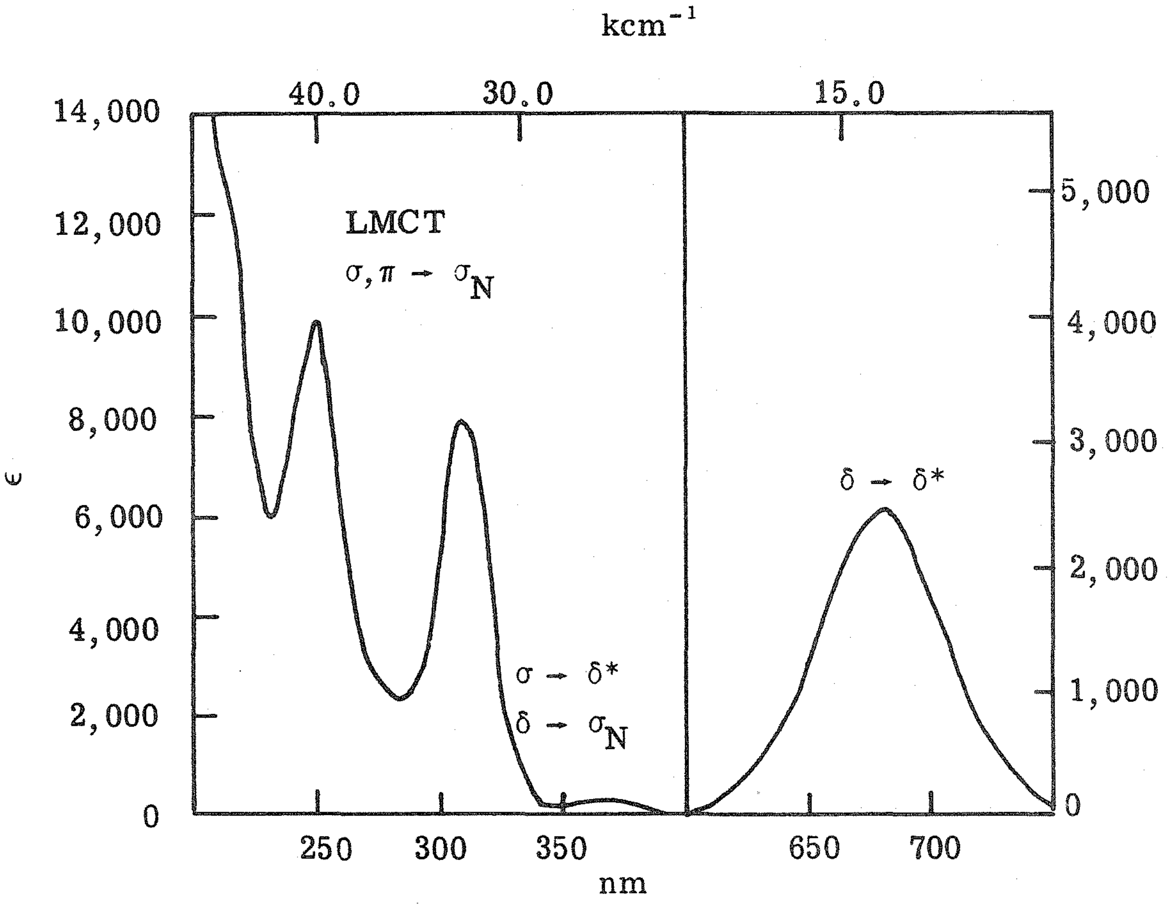


Figure IV-2. Electronic spectrum of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ in acetonitrile solution at room temperature.

available as a result of the spectroscopic study of Cowman, and the initial investigations were performed on these species. As rhenium(III) is in a relatively stable oxidation state, monomeric Re(III) complexes would not be expected to undergo the 4 electron process mentioned earlier. However, since the absorption spectra had been well worked out, they were ideal compounds on which to do the initial study. Hence, most of the work reported in this chapter will concern Re(III) dimers, and only the results of very preliminary investigations into the photochemical properties of Mo(II) dimers will be presented.

Experimental

Preparation of Compounds. $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ was prepared by the hypophosphorous acid reduction of potassium perrhenate.[14] The starting compounds for preparation of the Mo(II) dimers were $Mo_2(C_2H_3O_2)_4$, prepared by oxidation of $Mo(CO)_6$ with acetic acid,[15] and $[NH_4]_4[Mo_2Cl_8] \cdot NH_4Cl \cdot H_2O$, prepared from the acetate by the method of Brencic and Cotton.[16] $Mo_2Cl_4(PEt_3)_4$ was prepared from $[NH_4]_4[Mo_2Cl_8]$ by a vacuum line adaptation of the method of San Filippo.[17] $K_4[Mo_2(SO_4)_4]$ and $[Mo_2(aq)]^{4+}$ were prepared by the method of Bowen and Taube,[18] and $ReCl_4(CH_3CN)_2$ and cis-$[(CH_3)_3NH][ReCl_4(CH_3CN)_2]$ were made by the method of Rouschias and Wilkinson.[19] Except for $[Mo_2(aq)]^{4+}$, which was prepared and studied in situ, all complexes were isolated as crystalline salts. All manipulations with the air-sensitive Mo(II) compounds were conducted on a vacuum line under an inert gas.

Irradiation Procedures. The compound to be studied was dissolved in the appropriate solvent and placed in a 1 cm quartz spectrophotometer cell. A special inert gas cell was used for the Mo(II) dimers. The cell was placed in a thermostated cell holder in front of the appropriate lamp and filter combination, and was irradiated for a period of time. The absorption spectrum of the solution was recorded before, during, and after the irradiation. Several different lamp and filter combinations were used for the photolyses. A 1000 watt Hg-Xe lamp equipped with either a pyrex filter to remove the high energy uv radiation, or a selected Corning glass filter to isolate a particular spectral region was used for the majority of the irradiations. A 450 watt medium pressure Hg lamp equipped with appropriate filters was used for the 313, 366, and 436 nm irradiations. Finally, a low pressure Hg Ultraviolet Products circular lamp was used for the 254 nm photolyses. In one experiment a Spectra-Physics 125 He-Ne laser (632.8 nm; 90 mw) was used as the irradiation source.

Batch Photolysis Procedure. When it was necessary to prepare a large amount of photoproduct, a pyrex jacketed lamp well was used as the irradiation vessel. Approximately 500 ml of the solution to be irradiated was placed in the vessel and an inert gas purge affected by using a two-hole rubber stopper equipped with gas inlet and outlet tubes. The vessel was cooled with circulating tap water and stirred with a magnetic stirrer during the photolysis. In all cases the 1000 watt Hg-Xe lamp equipped with a pyrex filter was used in the irradiation. After the reaction was complete, as evidenced by the electronic absorption spectrum of the solution, the solution was evaporated to dryness, and the resultant solid was either recrystallized or chromatographed on silical gel. The best recrystallization solvents for $ReCl_3(CH_3CN)_3$ are CH_2Cl_2/ethyl ether. Chromatography of a photolyzed solution of $Re_2Cl_8^{2-}$ on silica gel gave $Re_2Cl_8^{2-}$ and $ReCl_3(CH_3CN)_3$ as the first and second bands, respectively, if CH_3CN was used as the eluting solvent. $ReCl_4(CH_3CN)_2^-$ would not elute with CH_3CN but could be removed from the silica gel by using CH_2Cl_2 as the solvent. Satisfactory analyses were obtained for $ReCl_3(CH_3CN)_3$ and trans-$[(CH_3)_3NH][ReCl_4(CH_3CN)_2]$. Anal. Calcd for $[ReCl_3(CH_3CN)_3]$: Re, 44.80; Cl, 25.59; C, 17.32; N, 10.11; H, 2.17. Found: Re, 44.50; Cl, 25.53; C, 16.99; N, 10.46; H, 2.32 Calcd for trans-$[(CH_3)_3NH][ReCl_4(CH_3CN)_2]$: Re, 39.60; Cl, 30.20; N, 8.93; C, 17.86; H, 3.40. Found: Re, 40.37; Cl, 30.48; N, 8.71; C, 17.69; H, 3.51.

Quantum Yield Determination. The quantum yield of photolysis of $Re_2Cl_8^{2-}$ in CH_3CN was determined at 313 nm using a merry-go-round apparatus and ferrioxalate actinometry. The radiation intensity was 1.79×10^{-8} Einsteins/min. Disappearance of $Re_2Cl_8^{2-}$ was monitored by measuring the decrease in absorbance of solutions at 680 nm.

Radiation Intensity Dependence and Quantum Yield Temperature Dependence Experiments. These experiments were performed using the 1000 watt Hg-Xe lamp. For the intensity experiment a filter combination consisting of a pyrex block and a Corning No. 7-54 filter was used, limiting the region of radiation to approximately 300-390 nm. Neutral density filters with an absorbance of 0.6, 0.9, and 1.2 were used to vary the radiation intensity. Identical 3 ml samples of $Re_2Cl_8^{2-}$ in CH_2CN in 1 cm quartz spectrophotometer cells were prepared and irradiated with the various neutral density filters. The disappearance of $Re_2Cl_8^{2-}$ was monitored by measuring 680 nm absorbance changes.

The temperature dependence experiments were performed in a similar manner using the pyrex and Corning No. 7-54 filter combination. The irradiated samples were held in a thermostated cell holder, and the temperature of the holder was varied from -12 °C to 54 °C by using a refrigerated-heated water bath. A similar experiment was performed using a Corning No. 3-68 filter, limiting radiation to $\lambda < 500$ nm.

Acetonitrile Concentration Quantum Yield Dependence Experiment. Solutions containing exactly 1.0×10^{-6} moles of $[(n\text{-}C_4H_9)_3N]_2$-$[Re_2Cl_8]$ in a 3 ml solution of CH_3CN/CH_2Cl_2 were prepared. The percent CH_3CN concentration in the solutions was varied from 0% to 100%. The solutions were placed in identical 1 cm quartz spectrophotometer cells and were irradiated in a merry-go-round apparatus using the pyrex filtered Hg-Xe lamp. The absorption spectrum of each solution was measured before and after irradiation. As usual, disappearance of $Re_2Cl_8^{2-}$ was monitored by measuring the decrease in absorbance at 680 nm.

Solvent Dependence of Photolysis Quantum Yield Experiment. Solutions of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ in alumina chromatographed and distilled acetonitrile, chloroacetonitrile, and propionitrile were prepared and the concentration adjusted to give an absorbance of exactly 1.0 at 680 nm. The absorbance at 366 nm was 0.16 in each sample. Exactly 3 ml of each solution was placed in a 1 cm quartz spectrophotometer cell, and the solutions were irradiated for 150 min in a 366 nm merry-go-round apparatus. The absorbance of each solution at 680 nm was then measured, and the decrease in absorbance for each solution was calculated. The relative quantum yields were determined by comparing the absorbance changes.

Substrate Interaction Experiments. To determine if there was interaction between any photochemically produced species and either N_2 or acetylene, a solution to be irradiated was prepared and placed in a special air tight spectrophotometer cell, and the solution was purged with the appropriate gas for 30 min and then sealed under an atmosphere of that gas. The solution was then irradiated with the appropriate lamp and electronic spectral changes followed. The same procedure was followed for the substrate dimethylacetylenedicarboxylate, except that a few drops of this species were added to the solution, and the spectrophotometer cell was sealed under argon.

Spectral Measurements. Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer using KBr pellets prepared from ir spectrograde KBr powder (MC and B). Electronic absorption spectra were measured using a Cary 17 spectrophotometer. Emission spectra were recorded on a Cary 81 Raman spectrophotometer fitted with a Spectra-Physics 125 He-Ne laser or on a Perkin-Elmer MPF-3A fluorescence spectrophotometer. Magnetic susceptibility measurements were performed on a Princeton Applied Research FM-1 vibrating sample magnetometer calibrated with $HgCo(SCN)_4$.

Results and Discussion

Photolysis of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$. The electronic absorption spectrum of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ in CH_3CN is shown in Figure IV-2. Irradiation of a 6×10^{-5}M solution of $Re_2Cl_8^{2-}$ in CH_3CN with a 1000 watt Hg-Xe lamp equipped with a pyrex filter results in the spectral changes shown in Figure IV-3. As the photolysis proceeds there is a smooth decrease in absorbance at 14.7 kcm^{-1} and conversion at higher energy to new bands at 36.4, 40.8, and 43.5 kcm^{-1}. The decrease in intensity of the 14.7 kcm^{-1} band ($\delta \rightarrow \delta^*$) suggests that the δ bond, and possibly the entire quadruple bond, is broken. Indeed, two monomeric products can be isolated from a preparative scale photolysis. The most abundant is an orange solid analyzing for $ReCl_3(CH_3CN)_3$ and possessing a room temperature magnetic moment of 1.60 B.M. This magnetic moment is very similar to that of other known monomeric Re(III) complexes.[19-21] A tan compound with electronic absorption and infrared spectra identical to those of an analyzed sample of trans-$[ReCl_4(CH_3CN)_2]^-$ [22] is isolated in much smaller yield. The isolation of two monomeric products gives clear evidence that the quadruple bond of $Re_2Cl_8^{2-}$ is

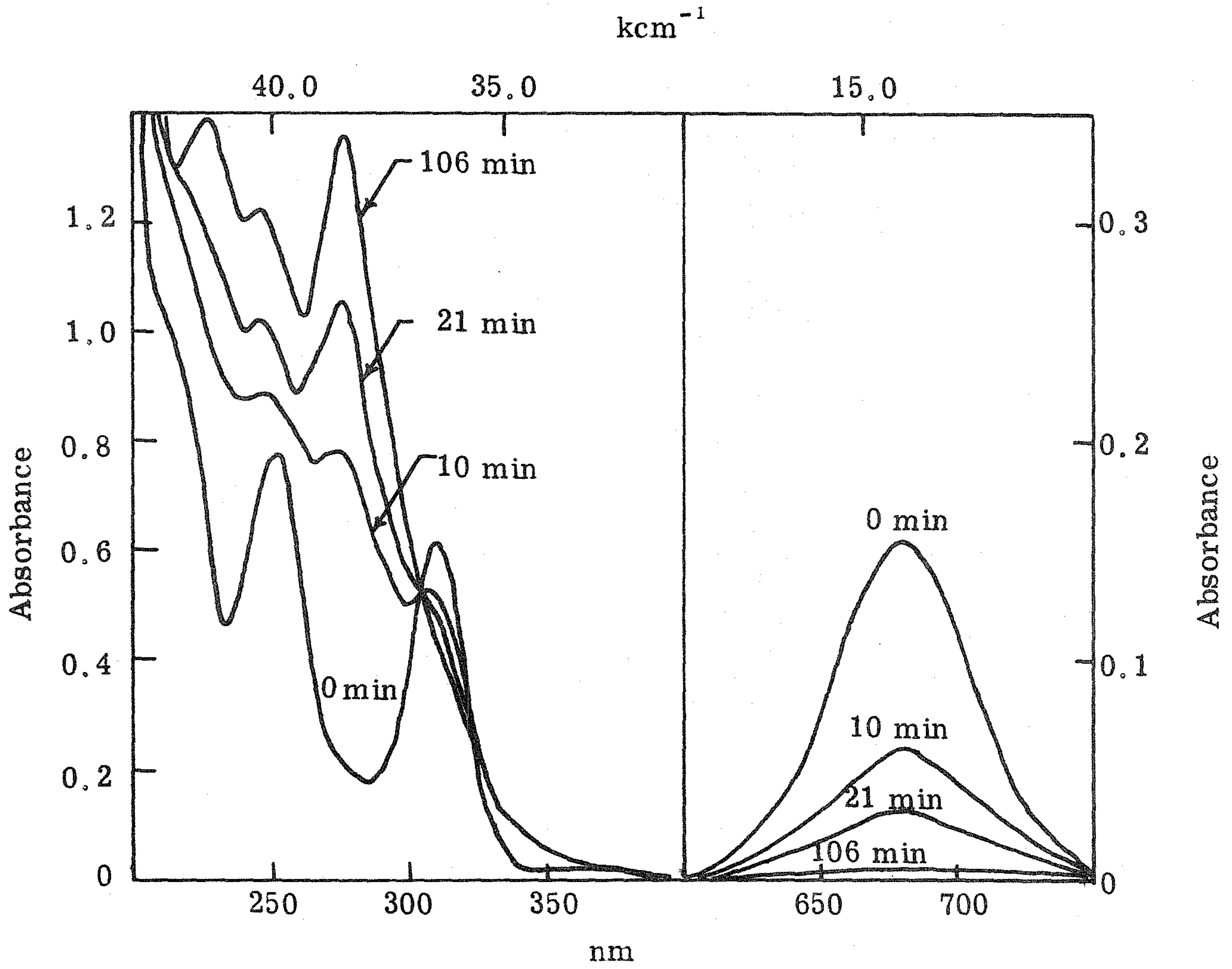


Figure IV-3. Irradiation ($\lambda > 300$ nm) of a 6×10^{-5}M solution of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ in acetonitrile.

broken photochemically. The disappearance quantum yield of $\mathrm{Re_2Cl_8}^{2-}$ upon 313 nm ($31.9\ \mathrm{kcm}^{-1}$) excitation at 25 °C, determined by monitoring the decrease in absorbance at $14.7\ \mathrm{kcm}^{-1}$, is 0.017 ± 0.005.

Irradiation of the tan compound from above in $\mathrm{CH_3CN}$ with pyrex filtered light ($\lambda > 300$ nm) results in a smooth and rapid conversion to $\mathrm{ReCl_3(CH_3CN)_3}$, but the spectral similarities of the two compounds have thus far precluded a quantum yield determination. However, the quantum yield of this reaction appears to be at least an order of magnitude greater than the disappearance quantum yield of $\mathrm{Re_2Cl_8}^{2-}$. Since it is difficult to visualize a one-step conversion of $\mathrm{Re_2Cl_8}^{2-}$ directly into $\mathrm{ReCl_3(CH_3CN)_3}$, the reaction pathway outlined below (Scheme 1) seems likely.

Scheme 1

$$\begin{tikzcd}
\mathrm{Re_2Cl_8}^{2-} \arrow[r, "\lambda > 300\ \mathrm{nm}", "\substack{\mathrm{CH_3CN} \\ \\ 1}"'] & 2\ \underline{\mathrm{trans}}\text{-}\mathrm{ReCl_4(CH_3CN)_2}^{-} \arrow[d, "2"', "\substack{\lambda > 300\ \mathrm{nm} \\ \mathrm{CH_3CN}}"] \\
 & 2\ \mathrm{ReCl_3(CH_3CN)_3}
\end{tikzcd}$$

The initial photoproduct under pyrex filtered excitation is *trans*-$\mathrm{ReCl_4(CH_3CN)_2}^{-}$, but this species is further photolyzed to $\mathrm{ReCl_3(CH_3CN)_3}$ under the conditions of the experiment. $\mathrm{ReCl_3(CH_3CN)_3}$ is isolated in much higher yield because the quantum yield of photolysis 2 is much greater than that of photolysis 1. Irradiation of $\mathrm{Re_2Cl_8}^{2-}$

in CH_3CN with higher energy 254 nm (39.4 kcm^{-1}) irradiation gives very complex spectral changes, indicating the occurrence of secondary and tertiary photoreactions. The initial spectral changes, however, do indicate that trans-$ReCl_4(CH_3CN)_2^-$ is formed. In fact, if a partially photolyzed solution of $Re_2Cl_8^{2-}$ in CH_3CN is chromatographed on silica gel, a very small amount of a tan compound is isolated, and this tan species is identical in all properties to the tan trans-$ReCl_4(CH_3CN)_2^-$ isolated under pyrex filtered excitation. It thus appears that trans-$ReCl_4(CH_3CN)_2^-$ is the primary photoproduct under both pyrex filtered and 254 nm (39.4 kcm^{-1}) excitation. However, this species then undergoes different photoreactions depending upon which irradiation source is used.

Photolysis of Monomeric Rhenium Complexes. In 1968 Rouschias and Wilkinson reported the preparation of cis-$Re^{III}Cl_4(CH_3CN)_2^-$ and $Re^{IV}Cl_4(CH_3CN)_2$,[19] and a study of the photochemical properties of these species has also been included in this investigation. The electronic absorption spectra of these and the monomeric complexes described in the previous section are shown in Figures IV-4 through IV-6, and the electronic absorption maxima and the infrared features are set out in Table IV-1. Irradiation of cis-$ReCl_4(CH_3CN)_2^-$ in CH_3CN with pyrex filtered excitation, followed by chromatography on silica gel, gives two photoproducts: $ReCl_3(CH_3CN)_3$ and trans-$ReCl_4(CH_3CN)_2^-$. As is the case with $Re_2Cl_8^{2-}$, it appears that the trans compound is formed first, and that it is then further photolyzed to $ReCl_3(CH_3CN)_3$. This is strongly indicated by the

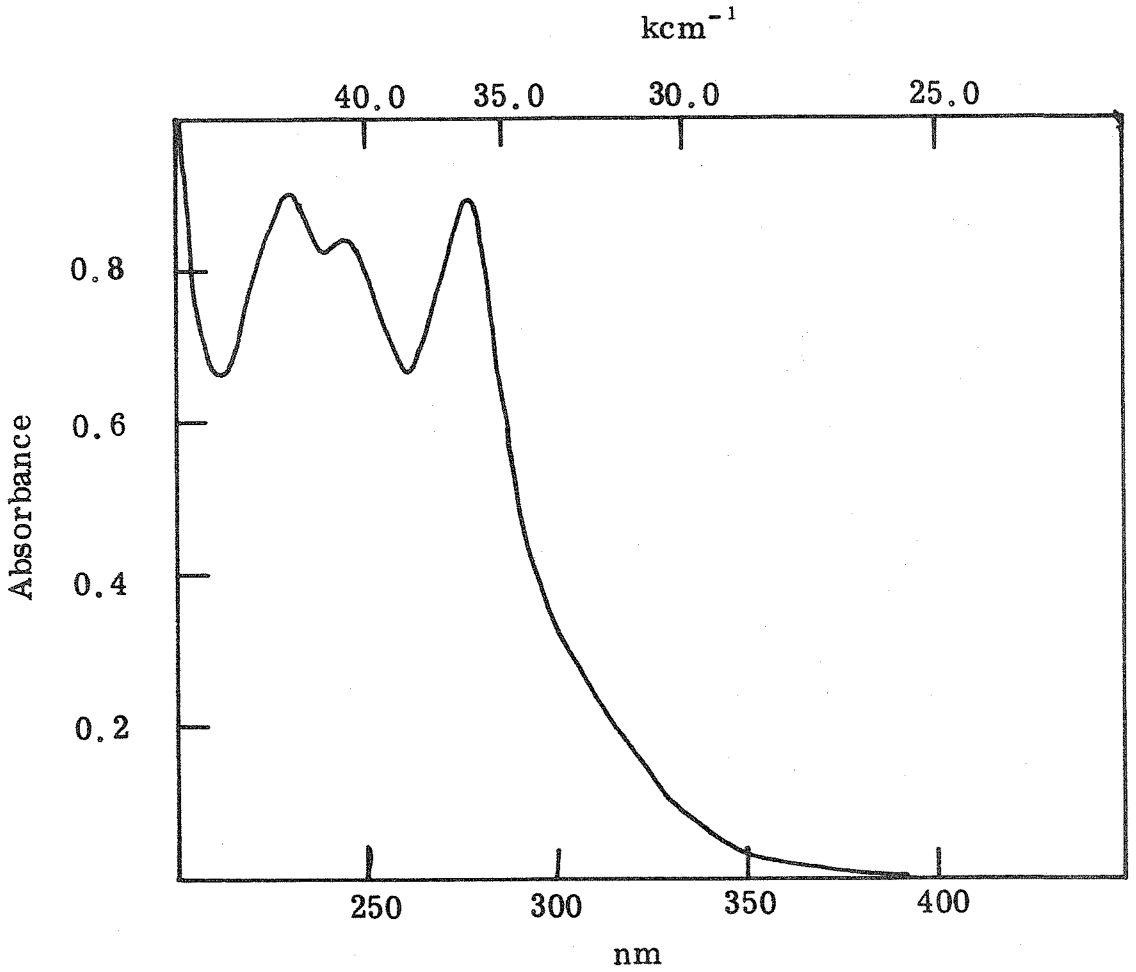


Figure IV-4. Electronic spectrum of $ReCl_3(CH_3CN)_3$ in acetonitrile solution.

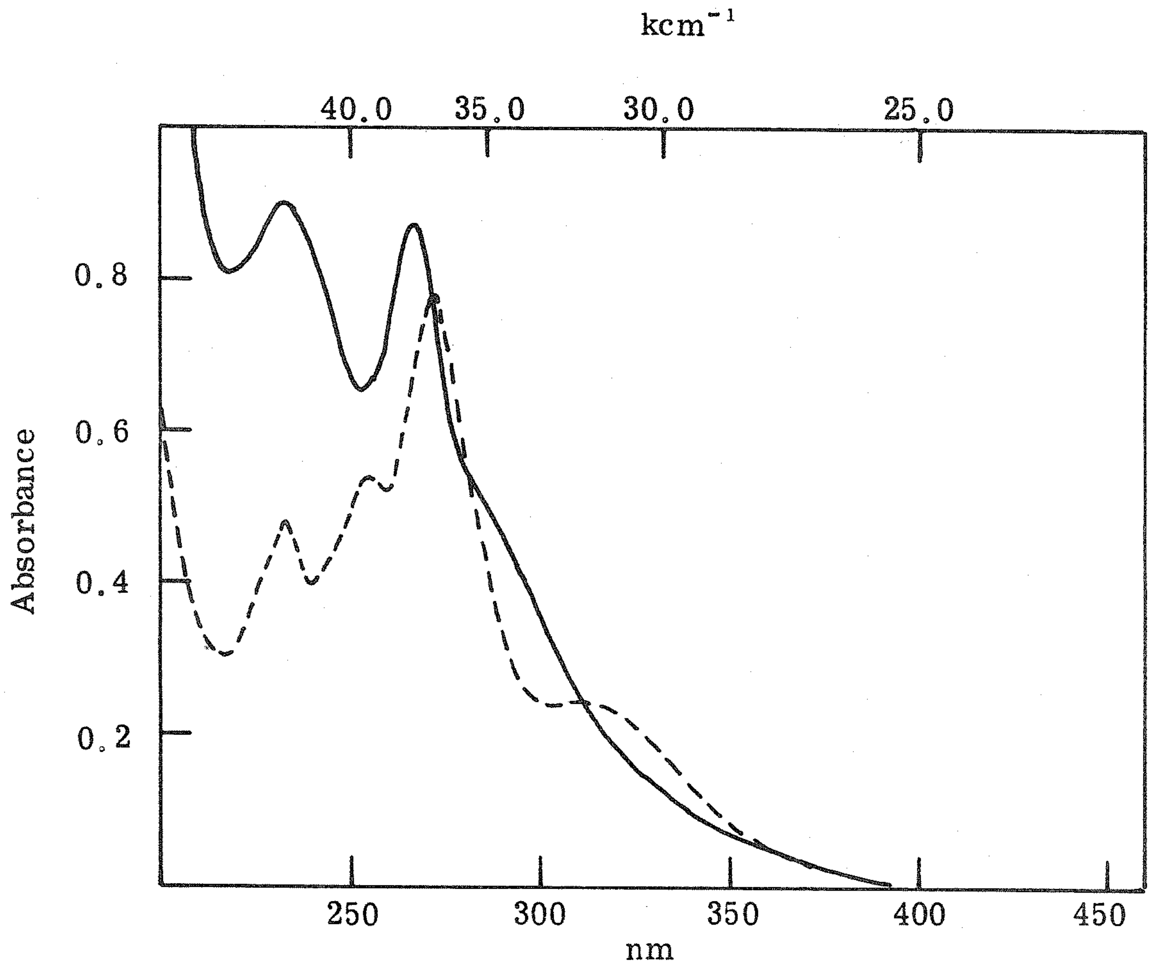


Figure IV-5. Electronic spectra of *cis*-[$ReCl_4(CH_3CN)_2$]$^-$ (——) and *trans*-[$ReCl_4(CH_3CN)_2$]$^-$ (---) in aceonitrile solution.

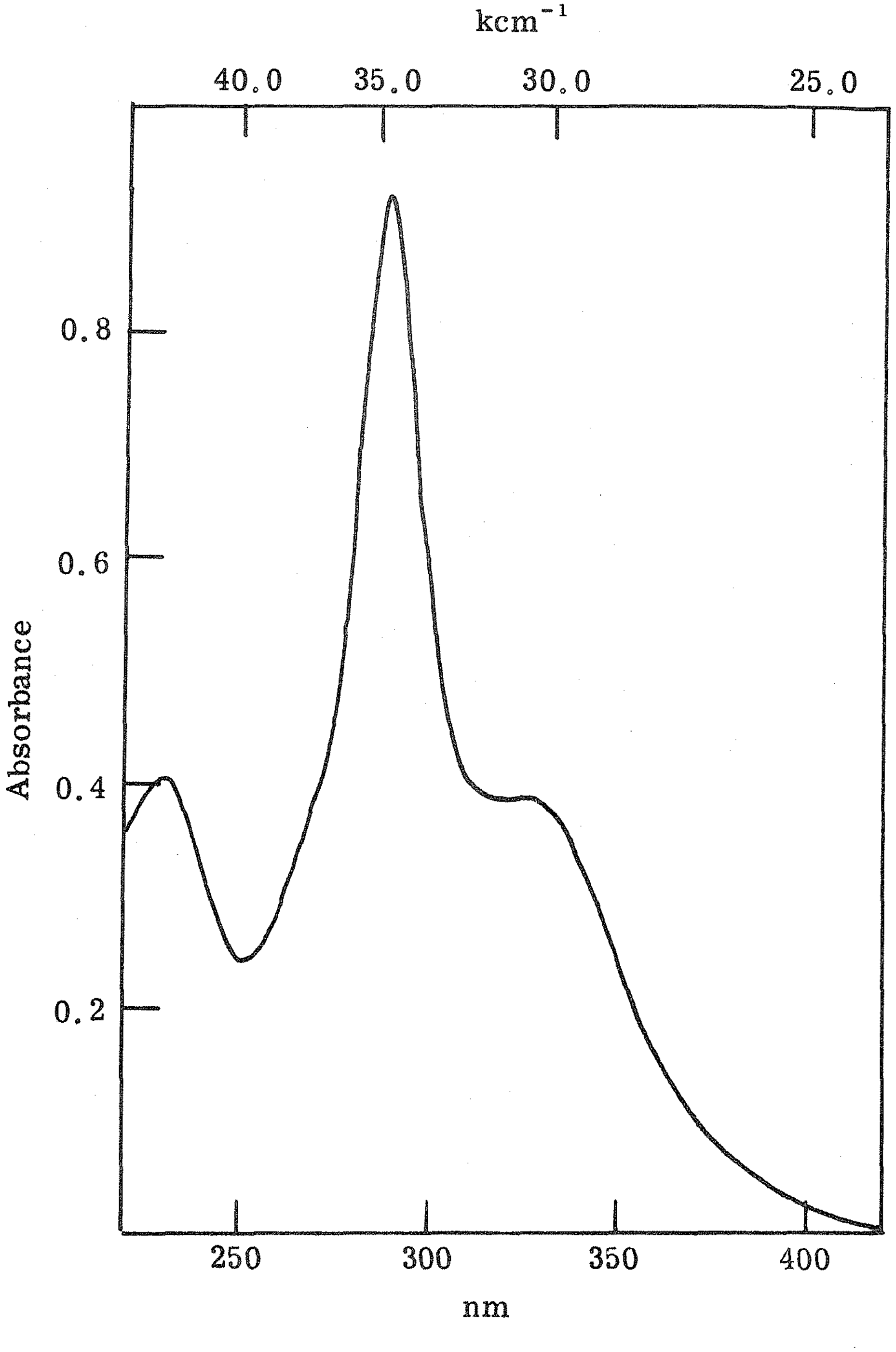


Figure IV-6. Electronic spectrum of $ReCl_4(CH_3CN)_2$ in acetonitrile solution.

Table IV-1. Infrared and Electronic Spectral Data for Some Re(III) and Re(IV) Complexes

	Infrared Maxima		Electronic Maxima[a]
Compound	cm^{-1}	Assignment	kcm^{-1}
$Re_2Cl_8^{2-}$	333[b]	ν_{Re-Cl}	14.7; 27.0; 28.3; 32.4; 39.7
$ReCl_3(CH_3CN)_3$	325[c]	ν_{Re-Cl}	32.3 sh; 36.4;
	315[c]	ν_{Re-Cl}	40.8; 43.5
	293[c]	ν_{Re-Cl}	
	d		
cis-$ReCl_4(CH_3CN)_2^-$	316 sh[b]	ν_{Re-Cl}	37.3; 42.6
	302	ν_{Re-Cl}	
	285	ν_{Re-Cl}	
	d		
trans-$ReCl_4(CH_3CN)_2^-$	301[b]	ν_{Re-Cl}	34.9 sh; 36.9;
	d		39.2; 43.1
$ReCl_4(CH_3CN)_2$	2313[c]	$\nu_{C\equiv N}$	30.8 sh; 34.8;
	2288[c]	$\nu_{C\equiv N}$	43.5
	325[c]	ν_{Re-Cl}	
	310[c]	ν_{Re-Cl}	
	d		

Table IV-1 (Continued)

[a] CH_3CN solution.

[b] Nujol mull.

[c] KBr discs.

[d] Peaks at 2970, 2911, 1405, 1355, 1015, 939, and 720 cm^{-1} attributable to coordinated CH_3CN.

observation that different ratios of the two products are obtained with different irradiation times, and in one experiment with a short irradiation time, only the trans compound was isolated.

Irradiation of cis-$ReCl_4(CH_3CN)_2^-$ in CH_3CN with 254 nm (39.4 kcm^{-1}) gives complex spectral changes. The initial changes, however, suggest that $Re^{IV}Cl_4(CH_3CN)_2$ is formed first and that it is further photolyzed to give unidentified products. In fact, 254 nm (39.4 kcm^{-1}) photolysis of $Re^{IV}Cl_4(CH_3CN)_2$ in CH_3CN produces the same complex spectral pattern produced by irradiation of cis-$ReCl_4(CH_3CN)_2^-$. It is interesting to note, however, that pyrex filtered excitation of $Re^{IV}Cl_4(CH_3CN)_2$ in CH_3CN gives no reaction.

When Wilkinson prepared $ReCl_4(CH_3CN)_2^-$ in 1968, he did not assign it the cis isomer.[19] The infrared evidence presented in Table IV-1 does suggest the assignment of a cis geometry to his complex and a trans geometry to the species isolated in the photolyses described above. A cis complex with C_{2V} symmetry has three ν_{M-Cl} ir-active modes ($2a_1$, b_1).[23,24] In the isomer assigned the cis geometry, three peaks are evident at 316, 302, and 285 cm^{-1}, and these compare well with the 315, 304, and 287 cm^{-1} bands in the established cis-$IrCl_4(py)_2^-$ complex.[25] A trans species has two ν_{M-Cl} ir-active modes ($2e_u$), although only one M-Cl stretch is observed in the trans-$ReCl_4(CH_3CN)_2^-$ isomer.[23,24]

A very puzzling feature of the ir spectra of all the Re(III)-acetonitrile complexes is the complete lack of a $\nu_{C\equiv N}$ peak. Even in concentrated nujol mulls or KBr pellets, $\nu_{C\equiv N}$ is not observed. Wilkinson noted the lack of $\nu_{C\equiv N}$ in the cis complex,[19] and in the related $ReCl_3(CH_3CN)(PPh_3)_2$ complex,[20] but did not give a truly satisfactory explanation of why it was missing.[20] It is conceivable that acetonitrile is bound edge-on through the π electrons of the C≡N bond, and that such interaction greatly reduces the C≡N bond order and leads to a large red shift and intensity decrease in $\nu_{C\equiv N}$. However, recent structural evidence, showing that the acetonitrile in $ReCl_3(CH_3CN)(PPh_3)_2$ is linear and coordinated through the nitrogen atom,[26] suggests that such is not the case. It appears that acetonitrile is coordinated end-on in each complex but that for some reason $\nu_{C\equiv N}$ is absent. It has been noted that in nitrile complexes of metal carbonyls $\nu_{C\equiv N}$ is very weak,[27] and in methylmercury cyanide it is entirely absent.[28] In the latter complex $\nu_{C\equiv N}$ is quite strong in the raman.[28] Unfortunately, raman spectra were not attainable on these Re(III)-acetonitrile complexes due to instrumental difficulties.

The electronic absorption spectra of the monomeric rhenium complexes are shown in Figures IV-4 through IV-6, and the spectral data are summarized in Table IV-1. Re(III) has a $\underline{d}^4$ electronic configuration and should exhibit several $\underline{d}$-$\underline{d}$ transitions. The least energetic of these come from the one electron excitations (assuming O_h rotation) $t_{2g}^4 \rightarrow t_{2g}^3 e_g$ and $t_{2g}^4 \rightarrow t_{2g}^4$, the latter representing a spin-pairing in the t_{2g} level. Although the spectra are not resolved well enough to make definitive assignments, it is attractive to postulate that the shoulders at 32.3 kcm^{-1} in the spectrum of $ReCl_3(CH_3CN)_3$ and at 31.7 kcm^{-1} in the spectrum of trans-$ReCl_4(CH_3CN)_2^-$ are due to $t_{2g}^4 \rightarrow t_{2g}^3 e_g$. This is particularly attractive since such an LF state would be predicted to lead to photosubstitution, as is observed in trans-$ReCl_4(CH_3CN)_2^-$. Photoexchange of CH_3CN could also be occurring in $ReCl_3(CH_3CN)_3$. It is unfortunate that no corresponding shoulder is observed in the spectrum of cis-$ReCl_4(CH_3CN)_2^-$.

Mechanistic Considerations. Several amplifying experiments have also been performed on the $Re_2Cl_8^{2-}$ system. No reaction was observed between the dimer and acetonitrile when solutions were stored in the dark or when refluxed for 12 h. This strongly indicates that the observed photochemistry is a true excited state process. An intensity experiment showed that the quantum yield of disappearance of $Re_2Cl_8^{2-}$ is independent of the radiation intensity (Figure IV-7), suggesting that the cleavage of the dimer is a one-photon process. The quantum yield of a two or three photon process should be directly proportional to the radiation intensity.

Some very important experiments were those in which the wavelength of irradiation was varied. Irradiation of $Re_2Cl_8^{2-}$ in CH_3CN at 632.8 nm (15.8 kcm^{-1}) with a 90 mw He-Ne laser, or with $\lambda > 580$ nm using the 100 w Hg-Xe lamp with a Corning No. 2-73 filter gave no observable photochemistry. This irradiation is into the lowest absorption band ($\delta \rightarrow \delta^*$), and this result strongly indicates that the lowest excited state is not photoactive. Even when the irradiation was

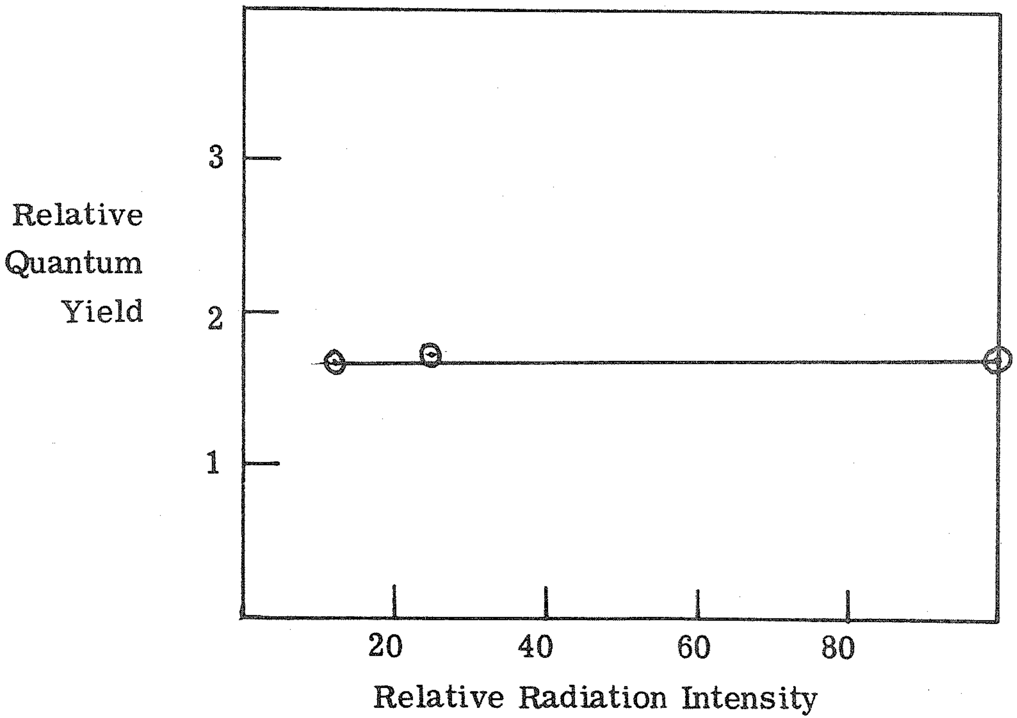


Figure IV-7. Plot of relative quantum yield of photolysis of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ in acetonitrile solution versus relative radiation intensity.

conducted on samples thermostated at 54 °C, no photochemistry was observed, indicating that the added thermal energy is not sufficient to lead to cleavage of the quadruple bond. Irradiation at 366 nm (27.3 kcm^{-1}) did induce the photoreaction. However, 436 nm (27.9 kcm^{-1}) irradiation of very concentrated CH_3CN solutions of $Re_2Cl_8^{2-}$ did not lead to reaction. These results indicate that the excited state that lies at about 27.0 kcm^{-1} is the active state. Assuming Cowman's interpretation of the absorption spectrum,[13] this band corresponds to $\sigma \rightarrow \delta^*$ and hence the photoactive state has the electronic configuration $\sigma^1\pi^4\delta^2(\delta^*)^1$. In such a state the formal bond order is reduced to three.

In general, the known photochemical reactions of most organic and inorganic compounds occur from the lowest excited states of the molecules. The lack of photochemistry from the lowest excited state in $Re_2Cl_8^{2-}$ is thus quite interesting and suggests that internal conversion between the upper excited states and the lowest state is not totally efficient. The energy gap between the active state at 27.0 kcm^{-1} and the lowest state at 14.7 kcm^{-1} is 12.3 kcm^{-1}, and this large energy separation may be responsible for the lack of 100% internal conversion. Interestingly, $Re_2Cl_8^{2-}$ is very weakly luminescent in the solid state and in solution. The emission spectrum obtained from the solid state at room temperature using a 632.8 nm (15.8 kcm^{-1}) exciting source is shown in Figure IV-8. The lowest absorption band is included to illustrate the degree of overlap of absorption and emission. An

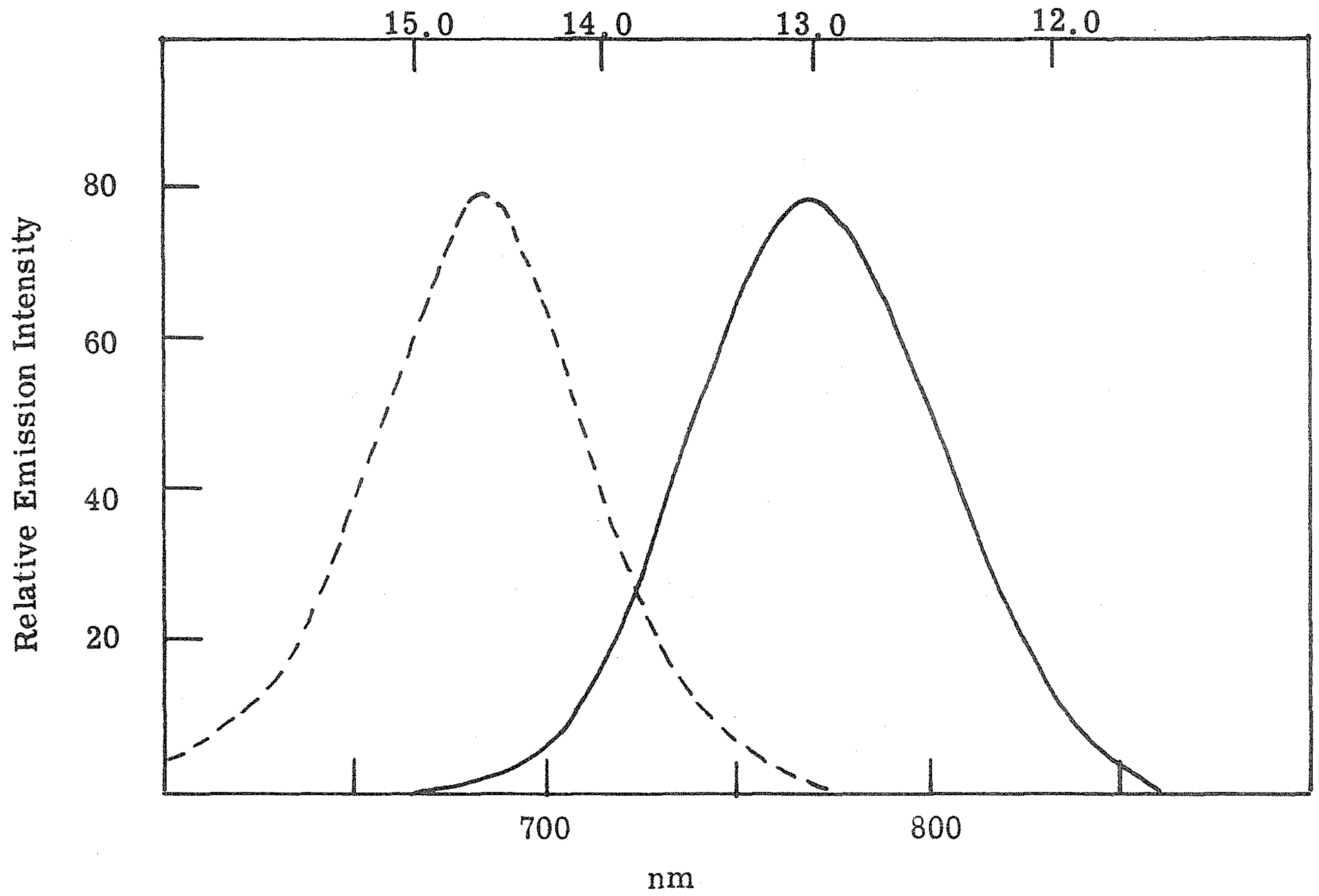


Figure IV-8. Room temperature solid state emission spectrum (——) and room temperature acetonitrile solution absorption spectrum (----) of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$.

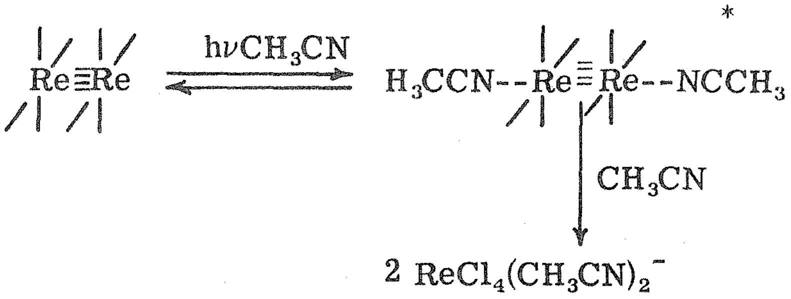
excitation spectrum of the solid sample diluted in a KBr pellet was obtained at 77°K, and surprisingly, the excitation spectrum corresponds closely to the absorption spectrum in band position and intensity.[29] This result indicates that internal conversion from the upper excited states to the lowest state is quite efficient.

Presumably, in acetonitrile solution at room temperature the molecule relaxes from the higher excited states to the state that lies at about 27.0 kcm^{-1}. Once this state is reached, two competing processes occur: relaxation to the lowest excited state at 14.7 kcm^{-1} and reaction to give cleavage of the quadruple bond. The excitation spectrum of the solid sample and the observation of luminescence from acetonitrile solutions at room temperature [29] indicate that the predominant process is relaxation to the 14.7 kcm^{-1} state and that only a very small fraction of the excited molecules give chemistry. This is consistent with the very low quantum yield (0.017) of photolysis.

Ideally, this author would like to present a detailed mechanism for the photochemical cleavage of the quadruple bond in $Re_2Cl_8^{2-}$. Essentially two possibilities exist. The first (Mechanism I) is that in the active excited state the dimer breaks apart into two $ReCl_4^-$ fragments which subsequently react with solvent to give the final products (Eq. 8):

$$Re_2Cl_8^{2-} \underset{k_1}{\overset{h\nu}{\rightleftharpoons}} 2[ReCl_4]^- \xrightarrow[CH_3CN]{k_2} 2ReCl_4(CH_3CN)_2^- \qquad (8)$$

For completeness a back reaction step with a rate constant k_1 is included. The second possibility (Mechanism II) is that in the excited state acetonitrile groups become loosely associated with the open coordination sites on the axis, and this association, possibly coupled with attack by other acetonitrile molecules, causes the dimer to fall apart directly into the products (Eq. 9):



(9)

Several experiments have been performed with the hope of elucidating the detailed photolysis mechanism. The first important experiment was to verify that there is little or no ground state interaction between the dimer and acetonitrile. Consequently, the absorption spectrum of the compound was measured in various solvents and the band positions were compared. Data for the $\delta \rightarrow \delta^*$ transition are summarized in Table IV-2. These data indicate that the position of the $\delta \rightarrow \delta^*$ transition is relatively insensitive to the nature of the solvent molecule, varying by only 75 cm^{-1}, and the small variance appears to be a function of solvent polarity. Thus it is very unlikely that solvent molecules are closely associated with the ground state molecule, especially since the solution spectra are very similar to the single crystal absorption spectrum.

Table IV-2. Electronic Absorption Maxima of the $\delta \rightarrow \delta^*$ Transition of $Re_2Cl_8^{2-}$ in Various Solvents

Solvent	λ_{max} kcm^{-1}	Dielectric Constant[a]	Dipole Moment Debye Units[a]
CH_3CN	14,663	37.5	3.37
CH_3NO_2	14,650	35.9	3.17
CH_3CH_2CN	14,641	27.2	3.56
CH_3COCH_3	14,641	20.7	2.72
$ClCH_2CN$	14,599	b	3.00[c]
CH_2Cl_2	14,588	9.1	1.55

[a] Except where indicated, data from reference 30.

[b] Not available.

[c] Reference 31.

If the cleavage of the quadruple bond requires thermal activation energy, as may be predicted for formation of the intermediate in Mechanism II, then the quantum yield of the photolysis should be temperature dependent. Hence, a temperature study was performed to test this hypothesis. The relative quantum yield of the photolysis of $Re_2Cl_8^{2-}$ in acetonitrile, using the 1000 w Hg-Xe lamp equipped with a Corning No. 7-54 filter, was measured at 54°C and -12°C using a thermostated cell holder. The quantum yield was identical at both temperatures, thus indicating that after absorption of light, no activation energy is required for the reaction.

Irradiation of $Re_2Cl_8^{2-}$ in CH_2Cl_2 gives no reaction. This is consistent with either Mechanism I or II. In Mechanism I it is doubtful that CH_2Cl_2 would react with the $ReCl_4^-$ fragments, and these fragments would simply dimerize to regenerate the starting material. In Mechanism II, it is unlikely that CH_2Cl_2 would attack the excited state, and the excited dimers would relax to the ground state giving no photochemistry. Irradiation of the dimer in mixed CH_3CN/CH_2Cl_2 solutions does give photochemistry. The quantum yield of disappearance of the dimer was measured in these solutions at different acetonitrile concentrations and the results are shown in Figure IV-9. These results indicate, but do not prove, that Mechanism II is the operating mechanism. If Mechanism I were operating, then at some relatively low acetonitrile concentration (e.g., 20%) every $ReCl_4^-$ fragment produced should be scavenged by acetonitrile. Hence, at and above this concentration, there would be

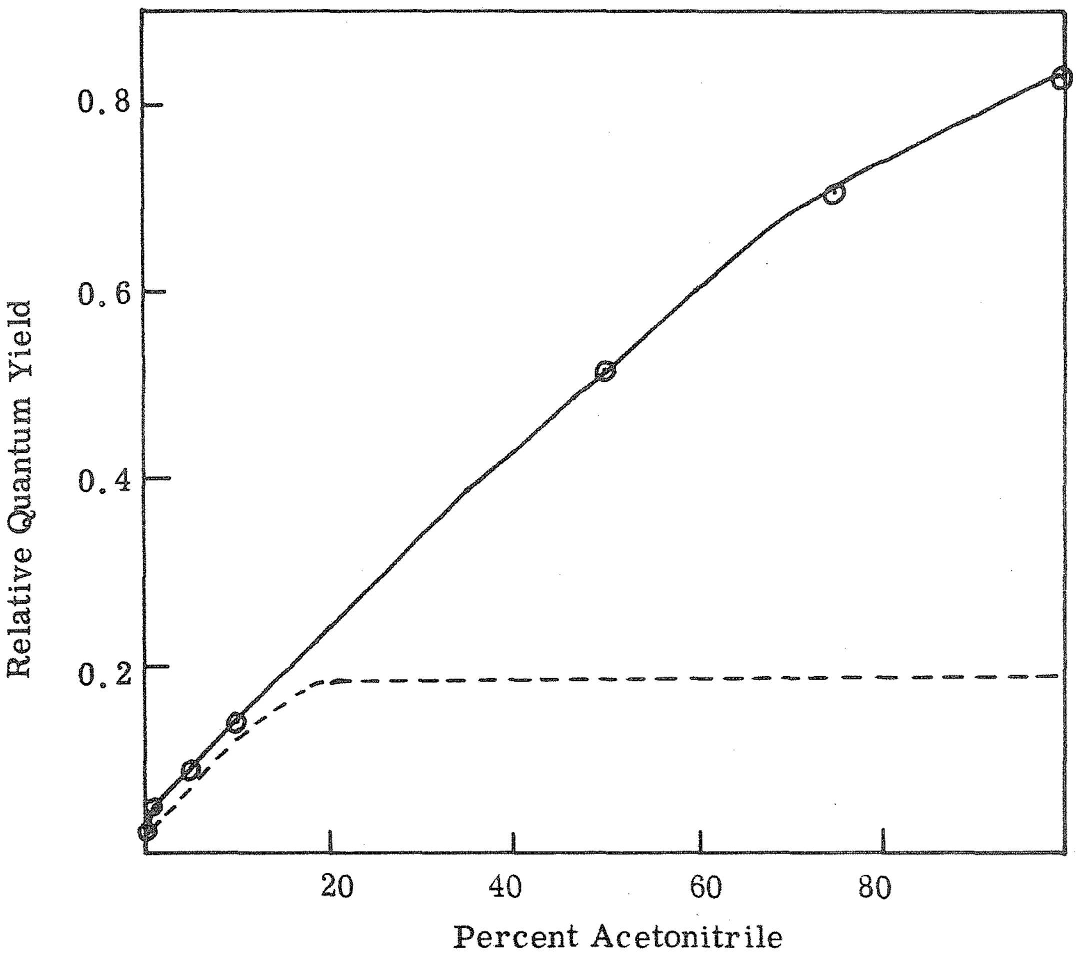


Figure IV-9. Relative quantum yield of disappearance of $Re_2Cl_8^{2-}$ versus solvent composition in acetonitrile/dichloromethane solution. The dashed curve represents the curve predicted if Mechanism I were operating.

no back reaction, and the quantum yield would cease to be a function of acetonitrile concentration. This is illustrated by the dashed curve in Figure IV-9. On the other hand, since Mechanism II is essentially an excited state quenching process, it is reasonable to assume that the quantum yield should be proportional to the acetonitrile concentration. Since the plot of experimental data shown in Figure IV-9 is close to linear throughout the acetonitrile concentration range, Mechanism II is indicated. It is not proved, however, as two factors could permit Mechanism I to give the experimental curve. First, if acetonitrile is not a very good scavenger for the $ReCl_4^-$ fragments, then it is conceivable that saturation of the quantum yield would not occur until very high acetonitrile concentration is reached. This possibility seems extremely unrealistic to this author, as acetonitrile is generally a good ligand for transition metals, and as reactive as the $ReCl_4^-$ fragments are expected to be, they should readily be scavenged by any CH_3CN present. Secondly, it can be argued that the large change in dielectric constant in going from 100% CH_2Cl_2 ($\epsilon = 9.08$) to 100% CH_3CN($\epsilon = 37.5$) markedly influences the quantum yield of cleavage of the quadruple bond into the $ReCl_4^-$ fragments. Hence the quantum yield determining factor is not the amount of back reaction occurring but the ability of the forward reaction to occur. Actually, this argument is not reasonable since the two negatively charged fragments would probably be less stabilized in a high dielectric constant medium. As stated earlier, this experimental result only suggests that Mechanism II is operating.

The quantum yield of disappearance of $Re_2Cl_8^{2-}$ relative to acetonitrile was measured in propionitrile and chloroacetonitrile, and the results based on the first 10% of reaction are summarized in Table IV-3. These results also strongly support Mechanism II. If Mechanism I were operating, and dipole moment and dielectric constant effects are neglected, in a neat coordinating solvent such as one of the three above, then every fragment produced would most certainly be scavenged by the solvent, and no back reaction would occur. In such a situation, the quantum yield should be independent of the nature of the solvent, and dependent only upon the intricate nature of the active excited state in the molecule. However, since the solvent plays a very important role of attacking the excited state in Mechanism II, if this mechanism is operating then the quantum yield should be very solvent dependent. Since the experimental results show the yield to be very solvent dependent, Mechanism II is indicated. Unfortunately, very little can be said concerning the effect of the dielectric constant since the constant for chloroacetonitrile was not found in the literature. However, it is doubtful that it is much greater than that of acetonitrile, and hence, it cannot account for the seven-fold increase in the quantum yield.

It was thought that a flash photolysis study would be extremely useful in elucidating the photolysis mechanism. Such a study was performed using a commercial Xenon Corporation flash photolysis apparatus capable of spectroscopically detecting intermediates with

Table IV-3. Quantum Yield of Disappearance of $Re_2Cl_8^{2-}$ in Various Solvents[a]

Solvent	Relative Quantum Yield	Dipole Moment[b] Debye Units	Dielectric[b] Constant
Acetonitrile	10	3.37	37.5
Propionitrile	3	3.56	27.2
Chloroacetonitrile	68	3.00[c]	--

[a] Irradiation was at 366 nm (27.3 kcm^{-1}). The quantum yields are expressed relative to acetonitrile which was arbitrarily assigned a value of 10.

[b] Data taken from reference 30, except where indicated.

[c] Reference 31.

lifetimes longer than 50 μsec.[32] Solutions of $Re_2Cl_8^{2-}$ in acetonitrile and in dichloromethane were flash photolyzed using this instrument, but in neither case was any intermediate detected. The very low quantum yield of photolysis of the dimer is not ideal for such a study and is presumably the reason that no intermediate of any kind was observed.

The available experimental results indicate, but do not clearly prove, that Mechanism II is the operating mechanism in the photochemical cleavage of the quadruple bond in $Re_2Cl_8^{2-}$. Although a detailed mechanism cannot be presented, the fact that the reaction occurs at all has important implications concerning the characteristics of the quadruple bond. Previous bond energy estimates in the range 300-400 kcal/mole[6,9] seem unreasonably high. If the mechanism involved simple dissociation to $ReCl_4^-$, photolysis at 366 nm (27.3 kcm^{-1}) would place an upper limit of 78 kcal/mole on the bond dissociation energy. However, the solvent undoubtedly plays an important role in the reaction and may lower the effective dissociation energy below that of the free ion. Such lowering could not be attributed to classical ionic solvation energy, as dissociation converts a doubly-charged anion to two singly-charged species. However, the monomeric ion is probably bound much more strongly than the dimer to acetonitrile molecules. If $Re_2Cl_8^{2-}$ is weakly bound to two acetonitrile molecules oriented along the Re-Re axis in the ground state, these molecules may become tightly bound and aid dissociation of the excited state. It is doubtful that more complex reorganization of the system could be involved since the reaction must occur during the very short lifetime of an upper excited state. It would be extraordinarily difficult to imagine interactions of this kind with the solvent which would lower the dissociation energy by more than 50 kcal/mole. Consequently, it is doubtful that the Re_2 bond energy in the dimer can exceed 130 kcal/mole. It is probably less.

Photolysis of Mo(II) Dimers. A very preliminary investigation into the photochemical properties of quadruply bonded Mo(II) dimers has been initiated, and the experimental results are presented here. Unfortunately, the very limited solubility of $K_4[Mo_2Cl_8]$, $[NH_4]_4[Mo_2Cl_8]$ and $Mo_2(C_2H_3O_2)_4$ has precluded a study of their properties, and $[(n\text{-}C_4H_9)_4N]_4[Mo_2Cl_8]$ has not yet been prepared. $Mo_2Cl_4(PEt_3)_4$ can be made[17] and is quite soluble in solvents ranging from acetonitrile to hexane. Unfortunately this species shows very little photochemistry even when solutions are irradiated with high energy 254 nm (39.4 kcm^{-1}) light. Only a very slow decomposition is observed. $Mo_2Cl_4(PEt_3)_4$ does luminesce, however. It shows a dim red emission from solid samples at room temperature, and a bright red emission from the solid state or frozen solutions at 77°K. The absorption, emission, and excitation spectra of this species are shown in Figure IV-10. By analogy to $Re_2Cl_8^{2-}$, the lowest band in the absorption spectrum at 17.0 kcm^{-1} is most likely the $\delta \rightarrow \delta^*$ transition. The 77°K emission band is a mirror image of the 17.0 kcm^{-1} band in the 77°K excitation spectrum, and the emission thus represents the $\delta^* \rightarrow \delta$ transition.

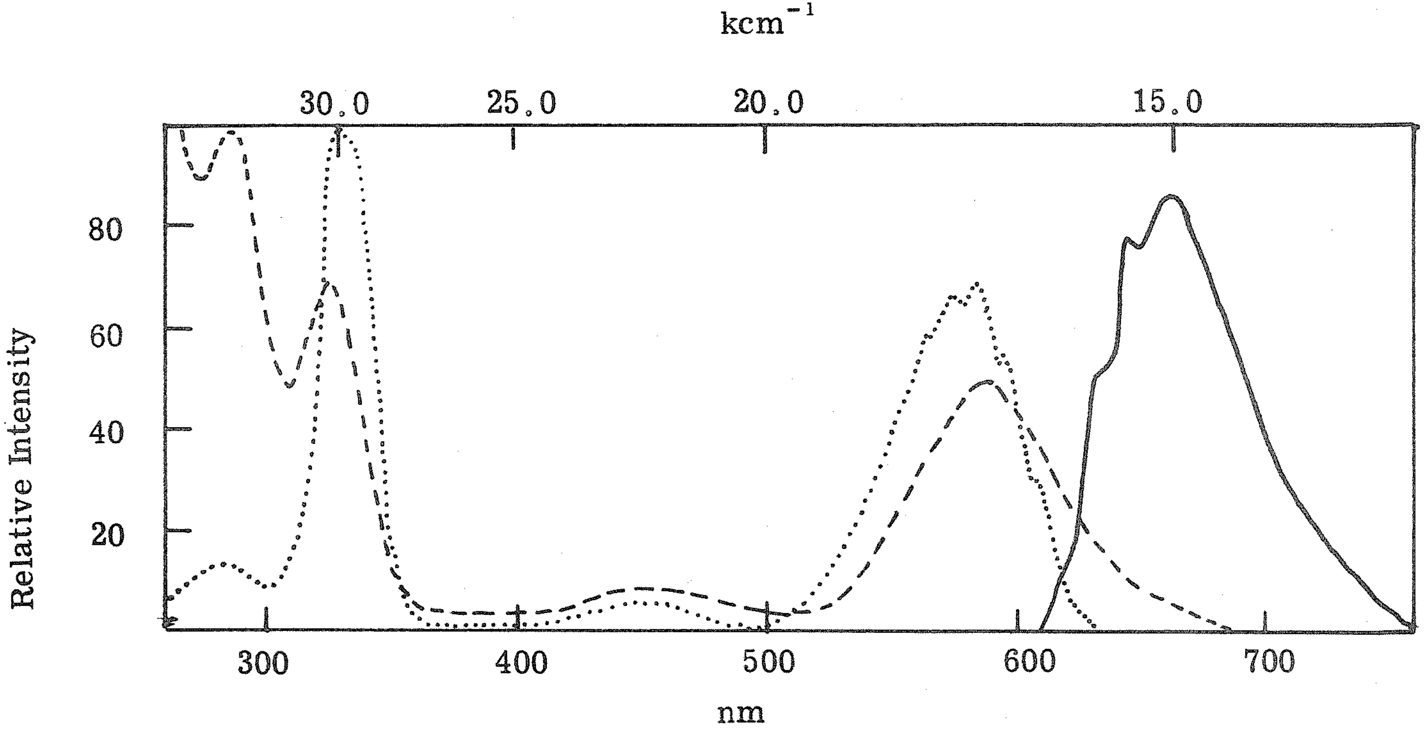


Figure IV-10. Uncorrected emission (——) and excitation (····) spectra of $Mo_2Cl_4(PEt_3)_4$ in EPA solution at 77°K. The electronic absorption spectrum (---) of $Mo_2Cl_4(PEt_3)_4$ in acetonitrile solution at 300°K is included for comparison.

It is interesting to note that the 326 cm^{-1} vibrational progression superimposed upon the emission band is less than the 334 cm^{-1} progression on the excitation band. By analogy to $Re_2Cl_8^{2-}$, this vibration is probably an A_{1g} metal-metal stretching mode.[13,33] A naive consideration would lead to the assumption that the metal-metal bond is stronger in the excited state than in the ground state, due to the greater vibrational spacing on the excitation band, and also on the absorption band.[13] However, there are several metal-chlorine stretching modes of A_{1g} symmetry,[33] and it is likely that there is very strong mixing with these modes and that the degree of mixing is greater in the excited state than in the ground state. This effect needs to be investigated in much greater detail. The observation of luminescence from this species, and the relatively small energy gap between the bands in the absorption spectra leading to efficient internal conversion, probably account for the lack of any photochemistry from this species.

In 1971, Bowen and Taube reported the preparation of $K_4[Mo_2(SO_4)_4]$ and $Mo_2(aq)^{4+}$,[18] and solutions of these species have been irradiated in this laboratory. Both compounds are stable only in deaerated aqueous acid media. The spectral changes which accompany 254 nm (39.4 kcm^{-1}) photolysis of $K_4[Mo_2(SO_4)_4]$ in argon purged 10 N H_2SO_4 are shown in Figure IV-11. During the photolysis many small bubbles of gas formed in the solution even though the irradiation cell was cooled by tap water in a special cell holder. This was a

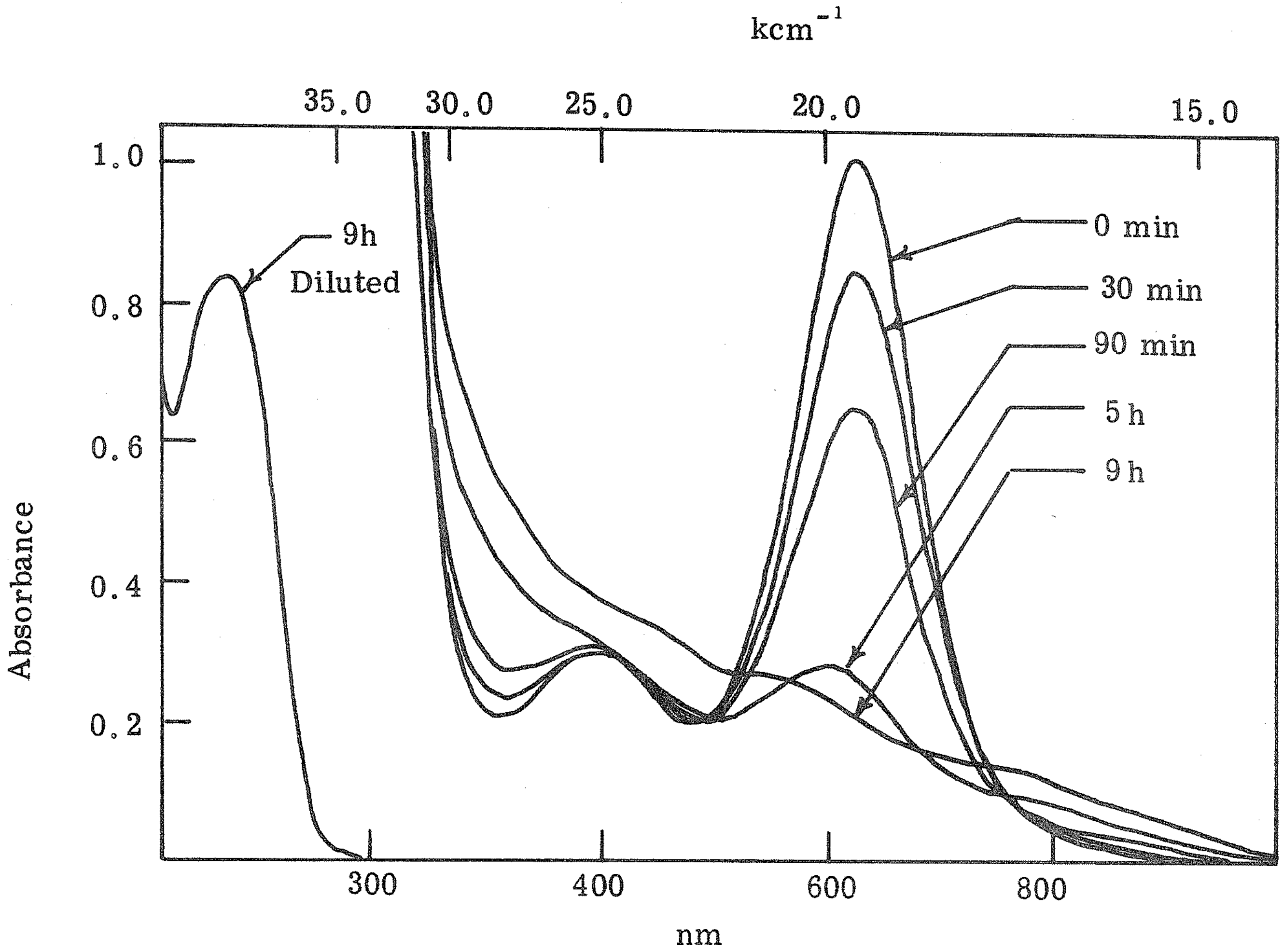
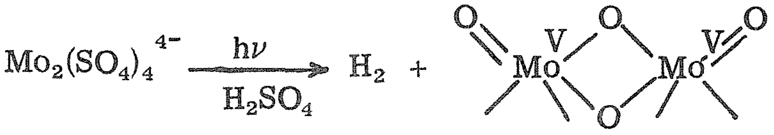


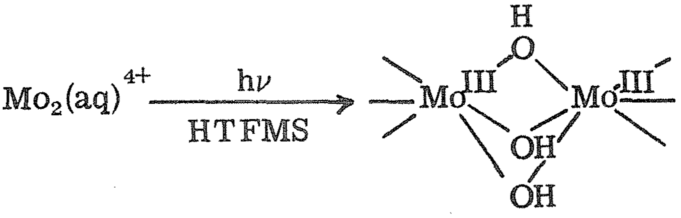
Figure IV-11. Spectral changes during 254 nm photolysis of $K_4[Mo_2(SO_4)_4]$ in 10 N H_2SO_4 at 300 °K.

clear indication that whatever photochemical reaction was occurring, it involved the formation of some gaseous species. The most likely candidates were H_2 and H_2S. An irradiated sample of $Mo_2(SO_4)_4^{4-}$ in H_2SO_4 was purged with argon and the purging gas was subsequently passed through a $CdCl_2$ solution. The lack of formation of any yellow CdS in this solution, and the lack of any detectable reaction of the gas with lead acetate paper, indicate that H_2S is not formed.[34] The presence of H_2 was confirmed by a gas analysis using vacuum line techniques. The gas was stripped off the irradiation vessel and passed through LN_2 traps to remove all water vapor. The volume of gas was measured by Toepler methods, the gas was cycled through a heated copper oxide tube, and the volume of the gas remeasured. The 70% decrease in the gas volume must have been accounted for by H_2 reacting with CuO to give H_2O. This was further evidenced by the collection of ice in an LN_2 trap between the CuO tube and the Toepler pump. The electronic absorption spectrum of the photolyzed solution is identical to the spectrum of a 10 N H_2SO_4 solution of $K_4[Mo_2(SO_4)_4]$ that has been oxidized by a stream of air. It is very likely that the air oxidized species is an oxobridged Mo(V) dimer, and this is supported by the similarity of the electronic spectrum to the spectra of known Mo(V) dimeric species. It thus appears that the photochemical reaction is as outlined in Eq. 10:



(10)

Irradiation of Mo_2^{4+}(aq) in 1 M trifluoromethylsulfonic acid (HTFMS) with 254 nm (39.4 kcm^{-1}) gives the spectral changes shown in Figure IV-12. The decrease in absorbance at 19.8 kcm^{-1} is an indication that the δ bond is broken, and the presence of the isosbestic points at 17.6 kcm^{-1} and 23.6 kcm^{-1} suggests a smooth conversion to a single product. The final spectrum shown in Figure IV-12 is identical to that of a green compound first prepared in 1957 by Hartman and Schmidt, and claimed to be $Mo(H_2O)_6^{3+}$.[36] However, Bowen and Taube have independently prepared and characterized $Mo(H_2O)_6^{3+}$ and have shown that the green Hartman and Schmidt compound must be something else.[18] Taube believes that the Hartman-Schmidt species is a hydroxy bridged Mo(III) dimer.[37] He formulates this opinion on the observations that the compound is diamagnetic, requiring either bridging ligands or a direct metal-metal interaction, and its ion-exchange behavior indicates coordinating hydroxy ligands. Thus it appears that the photochemical reaction is as outlined in Eq. 11:



(11)

Presumably H_2 is also formed in the photolysis, although no bubble formation was observed in the solution.

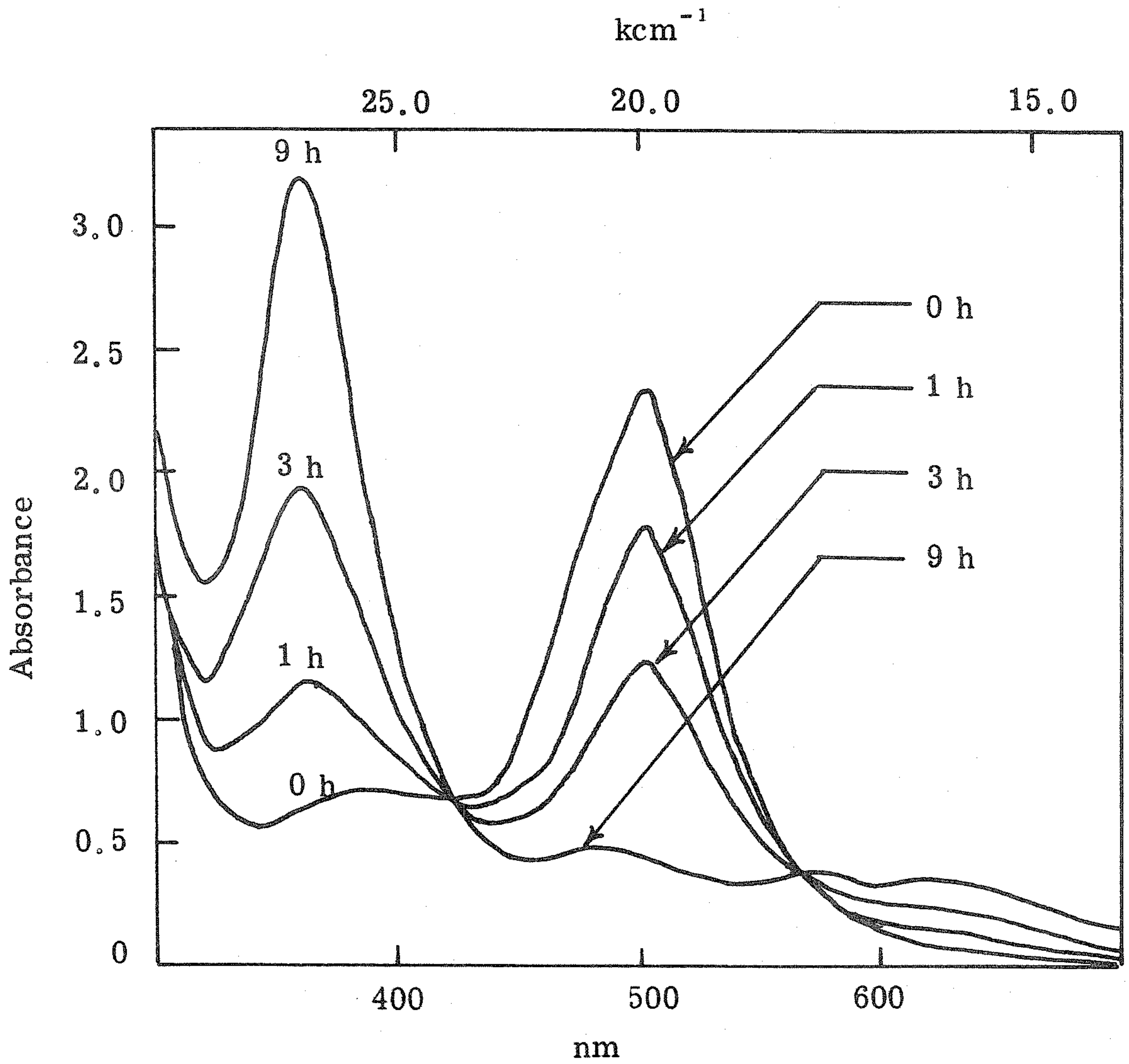


Figure IV-12. Spectral changes during 254 nm photolysis of $[Mo_2(aq)]^{4+}$ in 1 M HTFMS solution.

Irradiation of each Mo(II) dimer in acidic media results in a higher oxidation state complex as the ultimate product. At this point, a detailed reaction mechanism cannot be presented. However, one very attractive possibility exists: photolysis initially produces a monomeric Mo(II) complex, $Mo(H_2O)_6^{2+}$ or $Mo(SO_4)_2(H_2O)_2^{2-}$, and that Mo(II) is such a powerful reducing agent that it reduces water to give H_2 and higher oxidation state oxy or hydroxy complexes. Such a reactive monomeric Mo(II) unit is, of course, what is needed for the four-electron process described in the introduction to this chapter. An alternate photolysis mechanism is that irradiation induced photoelectron ejection occurs from the molybdenum atoms and that higher oxidation state complexes are generated directly. The ejected electrons could be scavenged by H^+ to eventually give H_2. This is a very real possibility since high energy 254 nm irradiation was used in this study.

It should be clear that the investigation into the photochemical properties of dimeric Mo(II) systems is only in a very preliminary stage and that much further work needs to be done. However, the results obtained to date are particularly encouraging and suggest that further studies will be fruitful.

Reaction of Re(III) and Mo(II) Species with Substrates. As was detailed in the introduction to this chapter, one of the original goals of this work was to photochemically generate very reactive species and hopefully observe unusual oxidative-additions and redox chemistry. With this in mind, irradiation of $Re_2Cl_8^{2-}$ has been carried out in the presence of N_2 and acetylene. Unfortunately, in neither case was there an effect on the reaction in acetonitrile, and no reaction was observed in CH_2Cl_2. It thus appears that there is no interaction between either an excited state of $Re_2Cl_8^{2-}$ or any photo-produced fragments with either N_2 or acetylene. However, if the irradiation is conducted in CH_2Cl_2 in the presence of dimethylacetylenedicarboxylate, then chemistry is observed. As the photolysis proceeds the $\delta \rightarrow \delta^*$ transition decreases in intensity and a broad absorbance increase occurs in the 22.2-33.0 kcm^{-1} region. The solution slowly acquires a pinkish color. Unfortunately, only a red oil is isolatable from the reaction mixture and a crystalline product was never obtained. Since irradiation of $Re_2Cl_8^{2-}$ under these conditions in the absence of the acetylene gives no reaction, it is attractive to speculate that some interaction between a rhenium species and the acetylene has occurred.

$K_4[Mo_2(SO_4)_4]$ and $[Mo_2(aq)]^{4+}$ have also been irradiated under an atmosphere of N_2, but no effect on the reaction was observed. An attempt was made to irradiate each of these species in the presence of dimethylacetylenedicarboxylate, but a very rapid thermal reaction occurred instead. Addition of the acetylene to an H_2SO_4 solution of $K_4[Mo_2(SO_4)_4]$ immediately caused the color to change from light pink to deep purple. Addition of the acetylene to an HTFMS solution of $[Mo_2(aq)]^{4+}$ gave an intense red color. Only a red oil was isolated, and the infrared spectrum of this oil showed it to contain a large amount of free dimethylacetylenedicarboxylate. The electronic absorption spectrum of the oil, shown in Figure IV-13, shows an intense transition at 23.8 kcm^{-1}. It is again attractive to postulate a Mo(II)-acetylene interaction and that the intense absorption is due to a MLCT transition.

Summary. It has been shown that irradiation of $Re_2Cl_8^{2-}$ in acetonitrile leads to cleavage of the quadruple bond and generation of monomeric Re(III) products. A better estimate of the quadruple bond energy has been obtained, and it was shown that previous estimates were high by at least a factor of two. Evidence has been presented suggesting that the quadruple bond in Mo(II) dimers can also be cleaved photochemically. Finally, although no proof of reactive species-substrate interaction has been obtained, evidence has been presented suggesting that such interaction is possible.

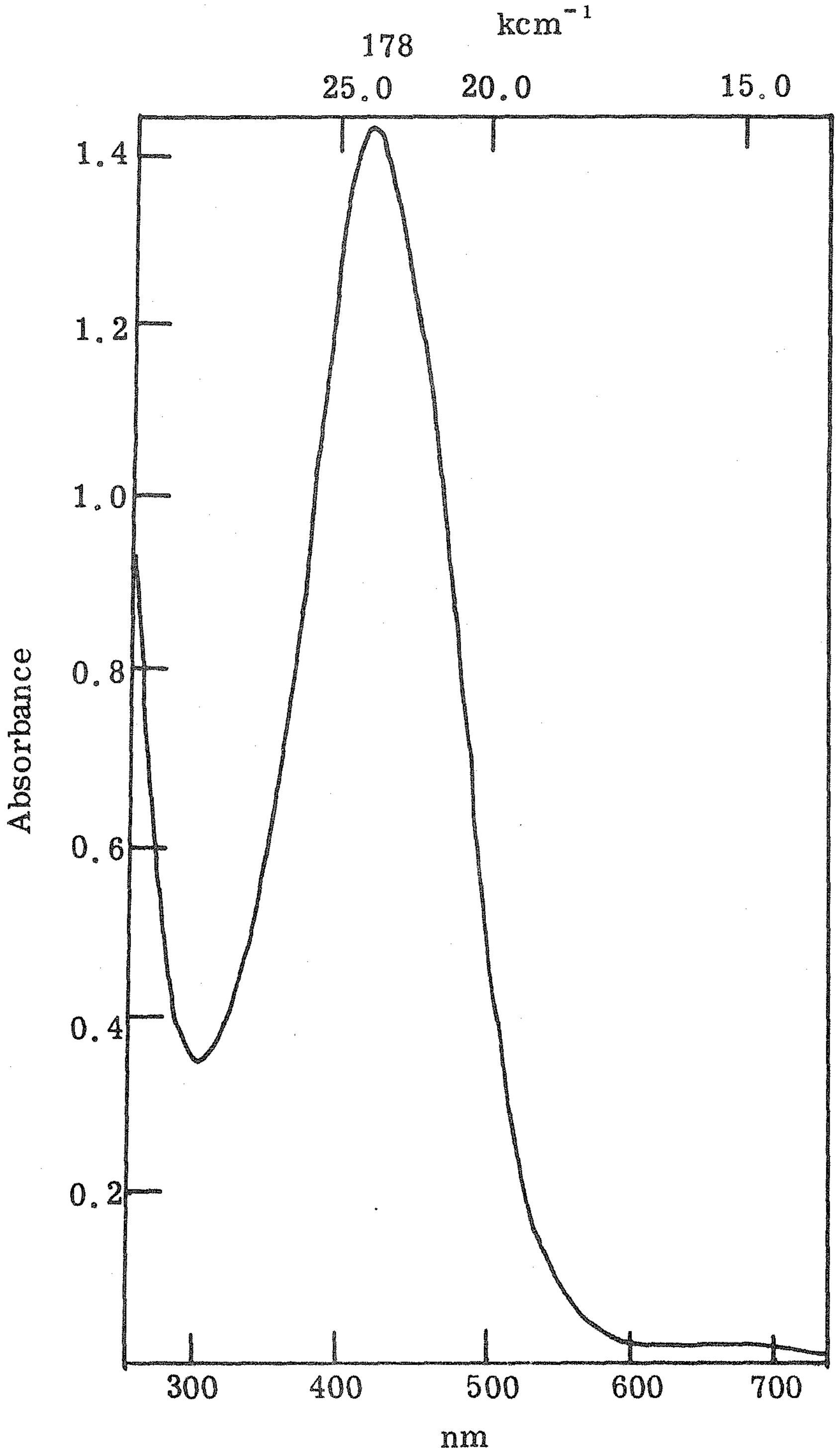


Figure IV-13. Electronic spectrum of the red oil obtained from the thermal reaction between $[\mathrm{Mo_2(aq)}]^{4+}$ and dimethylacetylenedicarboxylate.

References

1. P. W. Schneider, D. C. Bravard, J. W. McDonald, and W. E. Newton, J. Amer. Chem. Soc., **94**, 8640 (1972).
2. D. L. Kepert, "The Early Transition Metals," Academic Press, New York, 1972.
3. S. A. Hallock and A. Wojcicki, J. Organometal. Chem., **54**, C27 (1973).
4. M. Wrighton and D. Bredesen, J. Organometal. Chem., **50**, C35 (1973).
5. R. A. Levenson, H. B. Gray, and G. P. Ceasar, J. Amer. Chem. Soc., **92**, 3653 (1970).
6. F. A. Cotton, Accounts Chem. Res., **2**, 240 (1969).
7. F. A. Cotton and C. B. Harris, Inorg. Chem., **4**, 330 (1965).
8. F. A. Cotton, Inorg. Chem., **4**, 334 (1965).
9. F. A. Cotton and C. B. Harris, Inorg. Chem., **6**, 924 (1967).
10. F. A. Cotton, N. F. Curtis, B. F. Johnson, and W. R. Robinson, Inorg. Chem., **4**, 326 (1965).
11. F. A. Cotton, C. Oldham, and W. R. Robinson, Inorg. Chem., 5, 1798 (1966).
12. C. D. Cowman and H. B. Gray, J. Amer. Chem. Soc., **95**, 8177 (1973).
13. C. D. Cowman, Ph.D. Dissertation, California Institute of Technology, 1974.

14. F. A. Cotton, N. F. Curtis, and W. R. Robinson, Inorg. Chem., 4, 1696 (1965).

15. A. B. Brignole and F. A. Cotton, Inorg. Syn., 13, 87 (1972).

16. J. V. Brencic and F. A. Cotton, Inorg. Chem., 9, 346 (1970).

17. J. San Filippo, Jr., Inorg. Chem., 11, 3140 (1972).

18. A. R. Bowen and H. Taube, J. Amer. Chem. Soc., 93, 3287 (1971).

19. G. Rouschias and G. Wilkinson, J. Chem. Soc. A, 489 (1968).

20. G. Rouschias and G. Wilkinson, J. Chem. Soc. A, 993 (1967).

21. B. F. Figgis and J. Lewis, Progr. Inorg. Chem., 6, 152 (1964).

22. Prepared as described on page 146 from the photolysis of cis-$[(CH_3)_3NH][ReCl_4(CH_3CN)_2]$.[19]

23. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, 1970.

24. B. D. Catsikis and M. L. Good, Inorg. Chem., 8, 1095 (1969).

25. R. J. H. Clark and C. S. Williams, Inorg. Chem., 4, 350 (1965).

26. M. G. B. Drew, T. G. Tisley, and R. A. Walton, Chem. Commun., 600 (1970).

27. B. L. Ross, J. G. Grosselli, W. M. Ritchey, and H. D. Kaesz, Inorg. Chem., 3, 1023 (1963).

28. P. L. Goggin and L. A. Woodward, Trans. Faraday Soc., 62, 1423 (1966).

29. M. S. Wrighton, private communication.

30. J. A. Riccick and W. B. Burger, "Techniques of Chemistry. Organic Solvents," John Wiley and Sons, New York, 1970.

31. L. G. Wesson, "Tables of Electric Dipole Moments," MIT Press, Cambridge, Massachusetts, 1948.

32. These experiments were performed at California State University at Fullerton, California, using Professor Carl Wamser's Xenon Corporation flash photolysis apparatus.

33. W. K. Bratton, F. A. Cotton, M. Debeau, and R. A. Walton, *J. Coord. Chem.*, **1**, 121 (1971).

34. C. H. Sorum, "Introduction to Semimicro Qualitative Analysis," 3rd ed., Prentice-Hall, Englewood Cliffs, New Jersey, 1960.

35. P. C. H. Mitchell, *Quart. Rev.*, **20**, 103 (1966).

36. H. Hartman and H. J. Schmidt, *Z. Phys. Chem.*, **11**, 234 (1957).

37. H. Taube, private communication.

PROPOSITION I

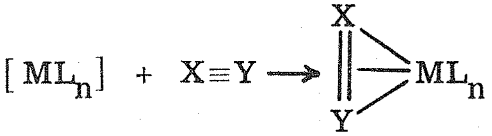
Generation of Reactive Species via the Photolysis of Metal-Metal Dimers and Metal Cluster Compounds

In Chapter IV of this dissertation it was shown that irradiation of $Re_2Cl_8^{2-}$ in CH_3CN results in cleavage of the quadruple bond and generation of monomeric Re(III) products. Evidence was also presented for photochemical cleavage of the quadruple bond in related Mo(II) dimeric complexes. As shown in detail on pages 131 - 134, the original goal of the research presented in Chapter IV was to photochemically generate very reactive, coordinatively unsaturated species. Some of the results obtained to date suggest that such species may indeed be formed, but as of yet no conclusive evidence has been found. I now propose to extend the study in Chapter IV to an extensive investigation of the photochemical properties of related dimeric and metal cluster compounds, with the specific goal of photogenerating extremely reactive species.[1]

The more stable compounds of transition elements at the left of the periodic table are generally those in which the metal is in a high oxidation state and consequently with a small number of d electrons. Monomeric complexes of the early transition metals in a low oxidation state exist only when the species contains strong π accepting ligands such as CO, CNR, phosphines, or arsines. When complexes are of low-valent early transition metals with ligands which are not π accepting (i.e., halides) are found, they invariably exist as dimeric or cluster compounds with strong metal-metal bonds. If it is possible to generate coordinatively unsaturated complexes of these low-valent metals that do not contain strong π-accepting ligands, then they should be extremely reactive and are expected to undergo chemical reactions which would lead to stabilization. One possible reaction, which is of little interest in this proposal, is that the coordinatively unsaturated species would dimerize or cluster to form strong metal-metal bonds. A second possibility is that the species would undergo redox chemistry to give an oxidized metal complex and a reduced substrate. A variation of this is that the species would react with a substrate capable of acting as a strong π-acceptor and some of the metal electron density could be delocalized onto the added ligand.

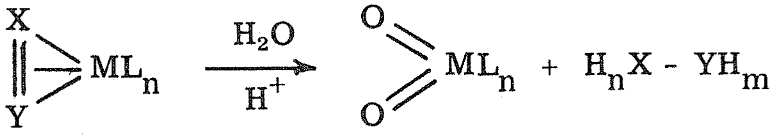
If such coordinatively unsaturated low-valent species can be generated, and if dimerization or clusterification can be prevented, then very interesting chemistry should be observed. This is especially true with species containing Mo(II) or W(II), as these electron-rich metals are expected to be extremely reactive and to undergo any reaction which would remove some of the electron density. Very importantly, it would not be unexpected to observe reaction between such species and normally inert molecules, thereby giving very unusual chemistry. I thus propose to try to generate such reactive species by photolyzing metal-metal dimers and metal cluster compounds, and then to study the reactivity properties of such species. In the next few paragraphs I shall discuss some of the chemistry expected for these reactive complexes and then discuss the different types of molecules that might give such species upon photolysis.

One of the more important reactions possible for a coordinatively unsaturated, electron-rich complex is simple addition to an unsaturated substrate $X{\equiv}Y$ (Eq. 1);



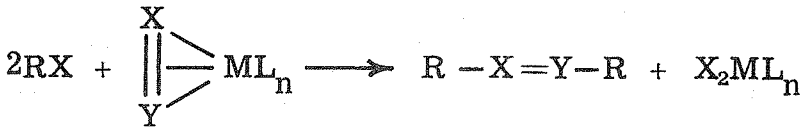
(1)

In this reaction $X{\equiv}Y$ could be acetylene, substituted acetylenes, nitriles, isonitriles, and possibly molecular nitrogen. Once the XY-metal complex is formed, a variety of reactions could be induced. An important one is hydrolysis to give an oxidized metal species and a reduced XY (Eq. 2):



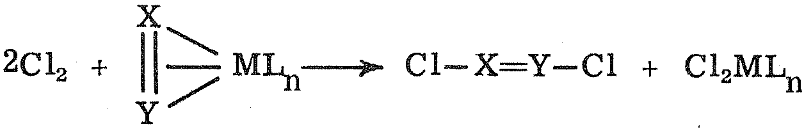
(2)

Since many of these low valent metal species would have a $\underline{d}^4$ electron configuration and a very stable $\underline{d}^0$ complex could be formed, the hydrolysis-reduction process is especially likely where four electrons can be transferred from the metal to the substrate. If, for example, $X{\equiv}Y$ represented molecular nitrogen, then hydrazine would be the final reduction product. It should also be possible to attack the XY-metal complex with electrophiles other than H^+. For example, generation of carbonium ions from secondary or tertiary alkyl halides in a suitable solvent system could lead to the reaction in Eq. 3:



(3)

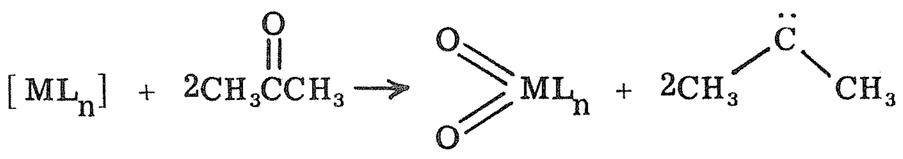
If X≡Y represented molecular nitrogen, this reaction would thus lead to formation of an azo compound. Another possible reaction is attack of the XY-metal complex by an oxidizing agent such as Cl_2 (Eq. 4):



(4)

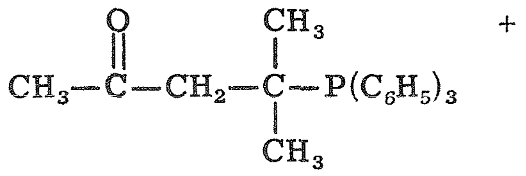
If X≡Y were acetylene, then 1,2-dichloroethylene would be the observed product.

Since early transition metals tend to readily form stable oxo complexes,[2,3] interesting reactions should occur with oxygen donor molecules. One such possibility is the abstraction of oxygen from acetone and formation of a carbene (Eq. 5):



(5)

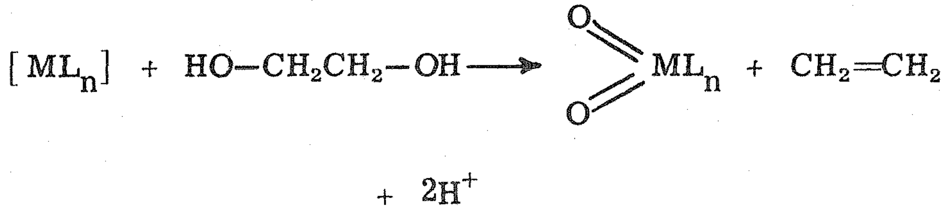
This reaction is especially likely for Mo(II) species. A precedent for this type of process does indeed exist, as $ReCl_5$ and β-$ReCl_4$ react with PPh_3 in acetone to give $ReOCl_3(PPh_3)_2$ and the DOTP cation,[4] where DOTP is 1,1-dimethyl-3-oxobutyltriphenylphosphonium, shown below:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-P(C_6H_5)_3 \quad +$$

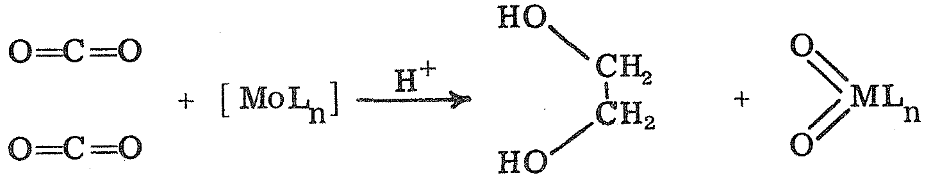
DOTP

Another possibility is that reaction could occur between the reactive metal complex and dialcohols leading to the formation of alkenes. For example, reaction of $[ML_n]$ with ethylene glycol could lead to oxygen abstraction and the formation of ethylene (Eq. 6):



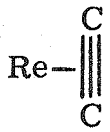
(6)

A very intriguing possibility, although not a likely one, is that reaction might be observed between such a reactive species and carbon dioxide to give an oxygen abstraction reaction similar to that shown in Eq. 7:



(7)

It should by now be obvious that the number of possible reactions between a photogenerated, low-valent, coordinatively unsaturated metal complex and organic substrate are quite enormous. It is only necessary to devise a procedure for generating such species, and several possibilities will now be considered.

As was shown in Chapter IV irradiation of $Re_2Cl_8^{2-}$ resulted in the formation of monomeric products. Although the mechanism of cleavage of the metal-metal bond is still uncertain, some of the evidence suggests that coordinatively unsaturated reactive fragments may indeed have been generated. This is illustrated by the observation that photolysis of $Re_2Cl_8^{2-}$ in CH_2Cl_2 in the presence of dimethylacetylenedicarboxylate leads to disappearance of $Re_2Cl_8^{2-}$ and formation of an intensely colored red species, suggesting a  $\mathrm{Re}-\begin{array}{c}\mathrm{C}\\ \vert\vert\vert\\ \mathrm{C}\end{array}$ interaction. The first experiments to be performed should be further investigations into the photolysis of $Re_2Cl_8^{2-}$ in CH_2Cl_2 in the presence of various organic substrates such as diphenylacetylene, alkenes, acetone, ethylene glycol, and various azo compounds. It will be necessary to isolate products in all cases and to carefully characterize each. This should be greatly facilitated by the use of high pressure liquid chromatography. The second step should be to carry out similar studies on various Mo(II) dimers where photochemical cleavage of the quadruple bond could generate reactive monomeric Mo(II) fragments. It will first be necessary to demonstrate that cleavage of the bond is possible, and then to look at interactions with organic substrates. A large number of Mo(II) dimers are known and such studies can be carried out in solvents ranging from toluene (for $Mo_2Cl_4(PEt_3)_4$[5]) to water (for $Mo_2^{II}(aq)^{4+}$[6]). Any photogenerated monomeric Mo(II) species should be extremely reactive and hopefully will give the unusual chemistry that is sought.

The photochemistry of several other dimeric systems should also be investigated in this study. The $Mo_2X_9^{3-}$, $W_2X_9^{3-}$, and $Re_2X_9^{-}$ ($X = Cl^-$, Br^-) anions are known to have the confacial bioctahedral structure shown in Figure 1,[7,8] and they are believed to possess some degree of metal-metal bonding. This is especially true in the case of $W_2Cl_9^{3-}$ for which the crystal structure has shown the tungsten atoms to be markedly displaced toward each other.[9] The metal-metal bonding has been formulated as consisting of a σ bond and two π bonds,[8] or alternately as three bonds resulting from overlap of the three t_{2g} orbitals on each metal.[10] The $Mo_2Cl_9^{3-}$ and $Re_2Cl_9^{-}$ anions also show metal-metal interaction,[7,10,11] but apparently not as strong as an $W_2Cl_9^{3-}$. The low energy electronic absorption bands of $Re_2Cl_9^{-}$ and $Mo_2Cl_9^{3-}$, summarized in Table I, have been assigned as transitions within the molecular orbitals formed by overlap of the t_{2g} metal orbitals.[12,13] Since the lowest excited states in these dimeric systems involve population of metal-metal antibonding orbitals, irradiation into these states could conceivably lead to cleavage of the bond and generation of monomeric Mo(III), W(III), and Re(IV) products. A Re(IV) species would probably not show unusual reactivity, but certainly such Mo(III) and W(III) species would. It should be noted that cleavage of the bond may not be possible because of the three chlorine bridges. It would also be worthwhile to investigate the photochemical properties of the mixed valence $Mo_2Cl_8^{3-}$[14] and $Re_2Cl_9^{2-}$[15] species.

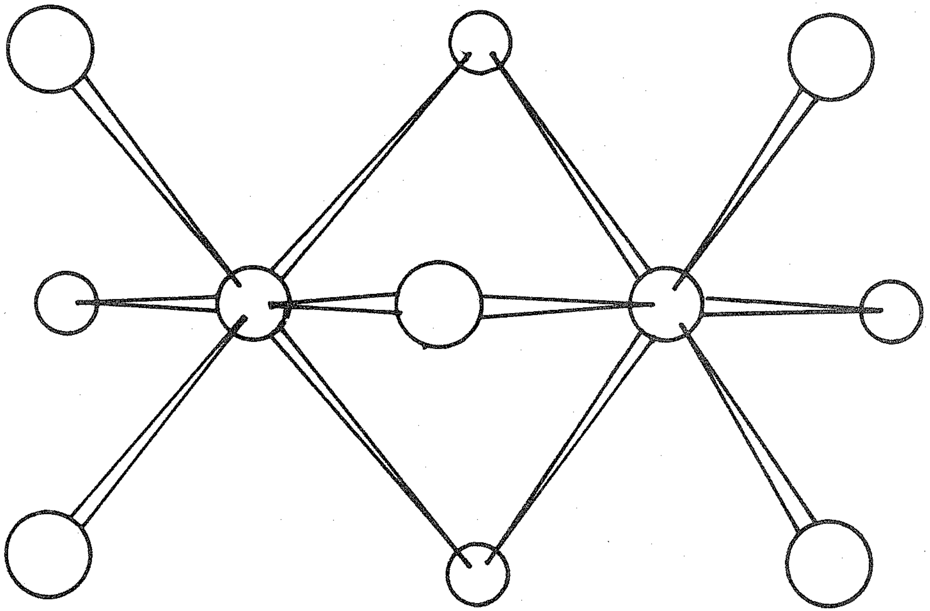


Figure 1. Confacial bioctahedral structure of $Mo_2X_9^{3-}$, $W_2X_9^{3-}$, and $Re_2X_9^{-}$.

Table I. Electronic Absorption Maxima for $Re_2Cl_9^-$ and $Mo_2Cl_9^{3-}$

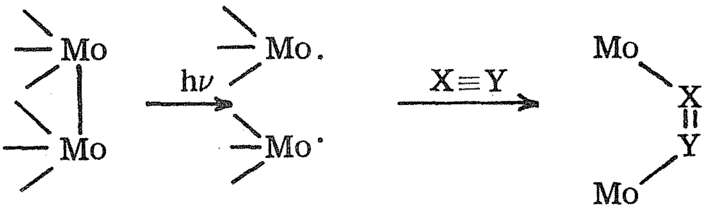
Compound	λ_{max} kcm^{-1}	Ref.
$Re_2Cl_9^-$	14.7	13
	18.9	
	24.4	
	26.0	
	27.4	
	27.9	
	30.5	
$Mo_2Cl_9^{3-}$	11.9	10
	12.4	
	13.0	
	13.4	
	15.2	
	15.3	
	16.6	
	19.7	

It is likely that low-valent reactive species can be generated via the photolysis of metal cluster compounds, and essentially three types of clusters should be investigated. These are the triangular Re_3X_9 clusters, the octahedral $M_6X_8^{4+}$ (M = Mo(II), W(II)) clusters, and the octahedral $M_6X_{12}^{n+}$ (M = Nb, Ta; n = 2, 3, 4) clusters. In each of these clusters the metal lies at the center of an approximately square MX_4 group, and the clusters are held together by strong metal-metal bonds and bridging halide ligands.[16] Cotton and Haas have formulated a molecular orbital description for these cluster compounds and give the energy level ordering as a function of the metal-metal distance.[16] When a ligand L is added to a solution of an Re_3X_9 cluster, an $Re_2X_9L_3$ adduct is formed. The electronic absorption spectra of these adducts are all very similar, and regardless of the nature of L, each shows bands around 13,000 cm^{-1} ($\epsilon = 750$) and 19,000 cm^{-1} ($\epsilon = 2,000$).[17-19] The independence of these spectral features upon L, and also on whether X is Cl^- or Br^-, strongly suggests that they are due to transitions within the Re_3 framework and hence involve the metal-metal bonds.[17] It is likely that the least energetic transitions in the $M_6X_8^{4+}$ and $M_6X_{12}^{n+}$ clusters also involve the metal-metal bonds.[20,21]

Irradiation of these cluster compounds could lead to several different types of reactions. One of the more probable, and one that is not of great interest in this proposal, is that simple photosubstitution of one of the ligands would occur. This would give a mixed XY cluster.

If irradiation disrupts some of the metal-metal bonding, as might be expected based on the previous discussion of the electronic structure, then the cluster could rearrange to give new and interesting clusters, or could undergo declusterification to yield very reactive fragments. It is the latter which would be most interesting to this proposal. For example, photolysis of Re_3Cl_9 could yield reactive monomeric [$ReCl_3$] species and $Mo_2Cl_8^{4+}$ could give [$MoCl_2$] fragments.

It can be argued that such declusterification is not possible because each metal atom is bonded to more than one neighbor in the cluster. This is especially true for the octahedral clusters where each metal is bonded to four nearest neighbors. This argument may be true, but a photoinduced disruption of the metal-metal bonding for just one pair of atoms could still yield a reactive species. For example, in a $Mo_6X_8^{4+}$ cluster, disruption of one Mo-Mo bond could open up a reactive site on each of the two molybdenums, and a substrate molecule could then react at this site. This is illustrated in Eq. 8 for one edge of the octahedron.



(8)

In summary, then, I propose that an attempt be made to generate extremely reactive, coordinatively unsaturated, electron rich species by photolyzing low-valent metal-metal dimers and metal cluster compounds, and then to investigate in detail reactions between such species and organic substrates.

References

1. C. D. Cowman has previously proposed that the photochemical properties of metal cluster compounds be investigated [C. D. Cowman, Ph.D. Dissertation, California Institute of Technology, 1973]. However, his proposal involved only a superficial investigation into the photochemical properties of these species with the primary goal of inducing molecular rearrangements to give new and novel types of cluster compounds. I am proposing to generate reactive species in the photolysis of metal-metal dimers and metal cluster compounds.
2. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," John Wiley and Sons, New York (1972).
3. D. L. Kepert, "The Early Transition Metals," Academic Press, New York (1972).
4. R. A. Walton, *Prog. Inorg. Chem.*, **16**, 9 (1973).
5. J. San Filippo, Jr., *Inorg. Chem.*, **11**, 3140 (1972).
6. A. R. Bowen and Henry Taube, *J. Amer. Chem. Soc.*, **93**, 3287 (1971).
7. P. F. Stokely, Ph.D. Thesis, Massachusetts Institute of Technology, 1969.
8. F. A. Cotton and D. A. Veko, *Inorg. Chim. Acta*, **6**, 161 (1972).
9. W. H. Watson and J. Waser, *Acta Cryst.*, **10**, 466 (1957).
10. R. Saillant, R. B. Jackson, W. E. Streib, K. Folting, and R. A. D. Wentworth, *Inorg. Chem.*, **10**, 1453 (1971).

11. M. J. Bennett, J. V. Brencic, and F. A. Cotton, *Inorg. Chem.*, **8**, 1060 (1969).

12. P. W. Smith and A. G. Wedd, *J. Chem. Soc. A*, 2447 (1970).

13. C. D. Cowman, Ph.D. Dissertation, California Institute of Technology (1973).

14. M. J. Bennett, J. V. Brencic, and F. A. Cotton, *Inorg. Chem.*, **8**, 1060 (1969).

15. F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, **6**, 223 (1967).

16. F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964); and references therein.

17. F. A. Cotton, S. J. Lippard, and J. T. Mague, *Inorg. Chem.*, **4**, 508 (1965).

18. F. A. Cotton and R. A. Walton, *Inorg. Chem.*, **5**, 1802 (1966).

19. J. E. Fergusson and B. H. Robinson, *Proc. Chem. Soc.*, 189 (1964).

20. M. B. Robin and N. A. Kuebler, *Inorg. Chem.*, **4**, 978 (1965).

21. P. B. Fleming and R. E. McEarley, *Inorg. Chem.*, **9**, 1347 (1970).

PROPOSITION II

A Study of the Reactivity of the Triplet State of the Nitrogen Molecule

The electronic structure of molecular nitrogen is well known and has been discussed by many workers.[1,2] The ground state has the electronic configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$, giving rise to a $^1\Sigma_g^+$ state.[2] The first excited state of N_2 has the electronic configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2(1\pi_g)^1$ and is a $^3\Sigma_u^+$ state. Gilmore[2] has calculated and plotted the potential energy surfaces for these and other states and they are shown in Figure 1. Table I displays the allowed and forbidden transitions in N_2 and their traditional nomenclature, and the electronic configurations of a few of the states are shown in Table II.

No dissociation continua have ever been observed for N_2 and no ionization continua exist above 796Å, corresponding to the first ionization potential of 15.58 ev.[3] The first transition observed with any significant absorption is the $X\,^1\Sigma_g^+ \rightarrow a\,^1\pi_g$ transition, whose (0-0) band is at 1450Å.[3] This band system contains the Lyman-Birge-Hopfield bands and continues down to about 1120Å.[3] The transition from the $^1\Sigma_g^+$ ground state to the $^3\Sigma_u^+$ excited state is dipole allowed but is highly forbidden by the change in the electron spin between the states.[4] From Figure 1 the (0-0) component of this transition is expected to occur at 49,850 cm^{-1} (200.6 nm). The transition has a very low absorption coefficient and only under very extreme conditions can

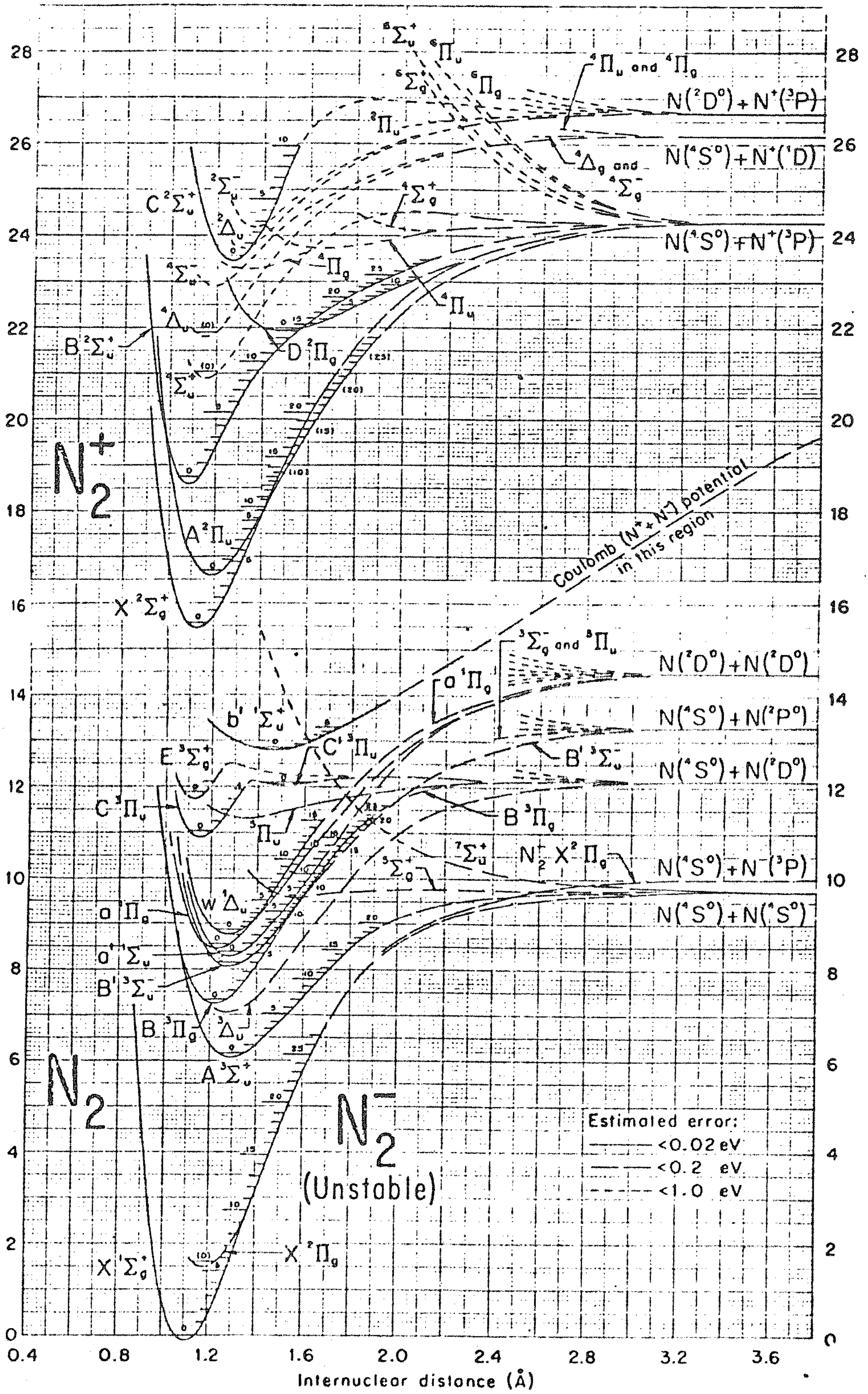


Figure 1. Potential-energy curves for N_2^-, N_2, and N_2^+ from reference 2.

Table I. Allowed and Forbidden Electronic Transitions in N_2.[a]

Permitted Transitions:

B ⇌ A	1st Positive Bands
C → B	2nd Positive Bands
C′ → B	Goldstein-Kaplan Bands
E → A	Bands
B′ → B	Y Bands
b′ → X	Birge-Hopfield Bands
A → X	Meinel Bands

Forbidden Transitions:

Z ⇌ X	Vegard-Kaplan Bands
a ⇌ X	Lyman-Birge-Hopfield Bands
B′ ⇌ X	Wilkinson-Ogawa-Tanaka I Bands
a′ ⇌ X	Wilkinson-Ogawa-Tanaka II Bands
C → X	Tanaka Bands

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[a] From ref. 2. The alphabetical designations refer to the states in Figure 1.

Table II. Electronic Configuration of Some States of N_2.[a]

	1_g	1_u	2_g	2_u	1_u	3_g	1_g	3_u	$3S_g$
$X^1\Sigma_g^+$	2	2	2	2	4	2	0	0	0
$A^3\Sigma_u^+$	2	2	2	2	3	2	1	0	0
$^3\Delta_u^+$	2	2	2	2	3	2	1	0	0
$B^3\pi_g$	2	2	2	2	4	1	1	0	0
$b'^1\Sigma_u^+$	2	2	2	2	3	2	1	0	0
$C^3\Sigma_u$	2	2	2	1	4	2	1	0	0
$E^3\pi_g^+$	2	2	2	2	4	1	0	0	1

[a] From ref. 2.

the light induced transition be observed.[4,5] However the ${}^3\Sigma_u^+$ and other higher energy triplet states can be populated in the laboratory by electric discharge and electron bombardment techniques.[6,7] The first observation of optical absorption by the ${}^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ transition was reported by Wilkinson in 1959.[8] Recently Shemansky has observed the absorption using very careful techniques and has determined the lifetime of the ${}^3\Sigma_u^+$ state.[4] He found that the state is split into two components, one with a lifetime of 1.27 sec and the other with a lifetime of 2.5 sec. Although this transition in absorption is highly forbidden, the corresponding luminescence band has been observed in gaseous discharges, in the spectrum of the night sky, and in the spectra of the auroras.[8]

Since molecular nitrogen is such an important constituent of the earth's atmosphere, any photochemical reactivity that it displays must be of importance. The photoreactivity of N_2 in its upper singlet states has been briefly investigated.[3] On the other hand there has been no study of the photoreactivity of triplet nitrogen.[9] In this proposition I propose to study the photoreactivity of the nitrogen molecule in its lowest triplet state with specific emphasis on an application to atmospheric chemistry.

There is presently evidence that triplet nitrogen is formed to some extent in the atmosphere[8,9] as evidenced by the observed emission from, and within, the triplet manifold. Although the absorption coefficient is extremely low for the ${}^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ transition, when one considers the atmospheric path length it is realized that there is a finite probability of some triplet nitrogen being formed by absorption of light. Molecular oxygen also has a region of absorption in the 50,000-65,000 cm^{-1} region where the nitrogen singlet to triplet transitions are expected to occur. Although the O_2 transition is also forbidden, it has a much greater absorption coefficient than the N_2 transition.[3] In a mixture of N_2 and O_2, the oxygen molecule would be expected to absorb essentially all the light in this spectral region. However, molecular oxygen is believed to be nearly completely dissociated into oxygen atoms in the atmosphere above about 80 km,[3,9] and oxygen atoms do not absorb light in this region.[3] Thus triplet nitrogen would be expected to be formed by irradiation only at altitudes near or greater than 80 km.

There is a very good possibility that N_2 triplets are formed by electron bombardment in the lower ionosphere at about 100 km altitude where the electron density is known to be about 10^4 electrons per cm^3.[3] In this region some of the electrons are known to have an energy of at least 4 ev and there is reason to believe that some may reach 6-7 ev.[9] Magnetic storms that occur in this region are known to increase the electron density and average electron energy.[3] In the event of such storms, the 10^4 electrons per cm^3 density has been shown to exist as low as 85 km.[3] Emission bands of molecular nitrogen are very prominent in the auroral spectrum.[3] Among the most intense bands in the visual region are those from the $B^3\pi_g \rightarrow A^3\Sigma_u^+$ transition, also called the First Positive System. The Second Positive System, $C^3\pi_u \rightarrow B^3\pi_g$, bands are prominent in the ultraviolet region, and the $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transition has also been observed[3] in auroral displays. Since the lower border of the auroral display often reaches down to an altitude of 80-90 km,[10] it is expected that triplet nitrogen would occur in this region. The above evidence indicates that the triplet levels of nitrogen can be, and are, populated in the atmosphere, but principally at elevations at or above 80 km. It is also reasonable to speculate that a small amount of triplet nitrogen is formed at very low levels of the atmosphere by electrical discharges (lightning). Since triplet nitrogen is known to have a long lifetime, and since most molecules in a triplet state are quite reactive, triplet nitrogen is probably a very reactive species.

In addition to the well known and often studied nitrogen cycle where nitrogen is taken up and returned to the atmosphere as molecular nitrogen, there is also an important cycle where nitrogen is returned to the atmosphere as nitrous oxide, N_2O.[11,12] The small amount of N_2O is produced along with large amounts of N_2 by bacteria in wet soil and in surface ocean waters.[11] The N_2O diffuses upward to 20-30 km where it reacts with singlet oxygen atoms as shown below:

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \qquad (1)$$

$$O(^1D) + N_2O \rightarrow NO + NO \qquad (2)$$

The singlet oxygen atoms are produced from the photolysis of ozone:

$$O_3 \xrightarrow{h\nu} O_2 + O(^1D) \tag{3}$$

The important reaction is the production of NO in reaction (2). NO will react further with ozone to produce NO_2, which in turn reacts with oxygen atoms to regenerate NO and produce O_2.

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{4}$$

$$NO_2 + O \rightarrow NO + O_2 \tag{5}$$

$$O + O_3 \rightarrow O_2 + O_2 \tag{6}$$

This reaction scheme is a catalytic cycle which destroys ozone. Since ozone is the only significant shield for the Earth against uv irradiation, its destruction is of great importance. It is noted that the destructive cycle begins with the decomposition of N_2O. The presently held belief is that all of the atmospheric N_2O comes from the Earth's surface.

I propose to study the reactivity of the nitrogen molecule in its triplet state with a specific goal of testing my hypothesis that some atmospheric N_2O is formed by the reaction of triplet nitrogen with either O_2 or atomic oxygen. As it does not seem reasonable to have all of the atmopsheric N_2O produced on the Earth's surface, this hypothesis presents a test case for studying the reactivity of triplet nitrogen.

An experimental set-up will have to be devised to produce nitrogen in its triplet state and then to test its reactivity with other small molecules. Although the 1894Å mercury line is a convenient irradiation source, I do not believe that light irradiation will suffice to produce $N_2({}^3\Sigma_u{}^+)$ due to the very low absorption coefficient of the ${}^1\Sigma_g{}^+ \rightarrow {}^3\Sigma_u{}^+$ transition. The best candidate would be either an electric discharge or electron bombardment. The former would be the easiest to construct but would have the disadvantage of producing other excited states of nitrogen in now unknown ratios. A particularly appealing experimental set-up which could be adapted for reactivity studies, is the one used by Borst and Zipf.[7] They passed N_2 under pressure past a 7.5 ev electron source and then into a detection chamber. They were studying the lifetimes of the rather shortlived $a\,{}^1\pi_g$ and $E\,{}^3\Sigma_g{}^+$ (115 and 190 μsec, respectively) states by this technique and interestingly enough were using the ${}^3\Sigma_u{}^+$ state as a reference signal because its long life meant it did not decay significantly in the passage time from the electron source to the detection chamber. For the reactivity studies, the detection chamber could contain the gas whose reaction with ${}^3N_2$ is being studied. Probably more realistic would be an experimental set-up with crossed molecular beams with ${}^3N_2$ in one beam and the other gas in the other beam. The gases in the beams would have to be traveling at low enough velocities to reduce the chance of reaction from vibrationally excited modes produced by molecular collisions. In testing my N_2O hypothesis, the "other" gas would be molecular oxygen, or possibly oxygen atoms produced from photolysis of O_2 by the 1894 Å mercury line. It would also be interesting to study the reactivity of ${}^3N_2$ with other gases such as O_3, NO, N_2O, NO_2, H_2O, etc. Gases collected during the experiment would have to be analyzed for reaction products. Recently gas chromatographic techniques have been developed for analyzing for trace amounts of "foreign" gas (including N_2O) in gas mixtures,[13-16] and these could be used in our experimental set-up.

In summary then I have proposed a study of the reactivity of the triplet states of molecular nitrogen. For a test case I have hypothesized that some atmospheric N_2O arises from reaction of triplet-nitrogen with O_2 or atomic oxygen. I have devised an experimental set-up for testing this hypothesis and for studying the reactivity of triplet nitrogen.

References

1. G. Herzberg, "Molecular Spectra and Molecular Structure, I: Spectra of Diatomic Molecules (2nd ed.), Van Nostrand Reinhold, New York (1950).
2. F. R. Gilmore, *J. Quant. Spectrosc. Radiat. Transfer*, **5**, 369 (1965).
3. R. A. Craig, "The Upper Atmosphere," Academic Press, New York (1965).
4. D. E. Shemansky, *J. Chem. Phys.*, **51**, 689 (1969).
5. P. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.*, **31**, 674 (1959).
6. N. P. Carleton and O. Oldenburg, *J. Chem. Phys.*, **36**, 3460 (1962).
7. a) W. L. Borst and E. C. Zipf, *Phys. Rev. A*, **3**, 979 (1971);
   b) W. L. Borst, *Phys. Rev. A*, **5**, 648 (1972).
8. P. G. Wilkinson, *J. Chem. Phys.*, **30**, 773 (1959).
9. Private communication from Dr. Oliver R. Wulf.
10. D. R. Bates in "Physics of the Upper Atmosphere," Academic Press, New York (1960).
11. H. Johnston, *Proc. Nat. Acad. Sci. (USA)*, **69**, 2369 (1972).
12. C. C. Delwiche, *Sci. Amer.*, **223**, 137 (1970).
13. C. T. Chiang, *Chung Kuo Nung Yeh Hua Hsueh Hui Chih*, **7**, 69 (1969).
14. R. M. Bethea and M. C. Meador, *J. Chromatogr. Sci.*, **7**, 655 (1969).
15. A. Zlatkis, H. R. Kaufman, and D. E. Durbin, *J. Chromatogr. Sci.*, **8**, 416 (1970).

16. J. R. Burford, *J. Chromatogr. Sci.*, **7**, 760 (1969).

PROPOSITION III

An Investigation into the Nature of the Manganese Ion in Naturally Occurring and γ-Irradiated Hilton Deposite Calcite

The mineral calcite, $CaCO_3$, often contains some percentage of Mn^{2+} substituted in the crystal lattice for the Ca^{2+} ion. In these minerals Mn^{2+} is coordinated by carbonate oxide ligands in a near octahedral geometry, and such manganese bearing calcites are known with up to 42 mole per cent $MnCO_3$.[1] When the Mn^{2+} concentration is only a few tenths weight percent, these minerals often show an orange-red luminescence when excited by uv irradiation or after γ-irradiation by cobalt 60.[2] The luminescence is believed to arise from de-excitation of Mn^{2+} from the $^4T_{1g}$ excited state to the $^6A_{1g}$ ground state.[3] Specimens from the vicinity of the abandoned optical grade calcite mining district known as the Hilton Deposit in northeastern San Diego County, California[4] are known to show an unusually intense, long-lived luminescence after γ-irradiation.[5] However, all luminescent properties have been shown to eventually disappear after such treatment.[5] I now propose to carry out detailed spectroscopic studies on samples of Hilton Deposit calcite in order to determine the fate of the manganese during and after γ-irradiation.

Emission spectrographic and atomic absorption analyses of representative specimens of Hilton Deposit calcite have shown the samples to contain 0.14% Mn or a mole fraction of $Mn/CaCO_3$ of

0.0025.[5] The optical absorption spectrum of this calcite has been measured and shows an intense ultraviolet transition centered at 310 nm and weakly shouldered at 401 nm.[5] The weak shoulder is very sharp, and based on the similarity to a 404 nm spectral feature in rhodochrosite, $MnCO_3$,[6] it has been assigned as the $^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g$ transition of Mn^{2+}.[5] The ultraviolet excited orange-red luminescence of natural samples of calcite has been well studied and is known to represent the $^4T_{1g} \rightarrow {}^6A_{1g}$ emission of Mn^{2+}.[3] The observed luminescence is centered at 608 nm and is quite broad.

When minerals are exposed to moderately high dosages of γ-irradiation valence electrons of atoms in the crystal are ejected from the atomic energy levels and can move about in the crystal lattice. Such electrons eventually are trapped in various lattice sites or induce oxidation-reduction reactions in some of the ions in the crystal. After irradiation, thermal energy allows some of the electrons to again move through the lattice and recombine with the ions formed by the irradiation. Often this recombination leaves the atomic species in an electronically excited state, and the energy released in relaxation to the ground electronic state can appear in the form of visible luminescence. Such is the case with γ-irradiated Hilton Deposit calcite. Although most calcites luminesce after cobalt-60 γ-irradiation, the Hilton Deposit calcite is unusual as the emission is extremely intense and is very long-lived, decaying over a period of several hours at room temperature.[5,7] The intense luminescence has been observed with samples subjected to dosages between 200 rads and 10 M rads. The γ-irradiated luminescence spectrum of a specimen of this calcite, recorded within one hour after irradiation, is shown in Figure 1.[5,7] The principal emission is centered at 608 nm, characteristic of Mn^{2+}, and minor peaks are at 408, 437, and 548 nm. Although the emission intensity decay curve is complicated, the effective half-life for the first several hours of luminescence is about one hour.[5] Curiously, if γ-irradiated specimens are stored for several days so that the irradiation damage can heal, the specimens lose all luminescent properties. Luminescence is no longer observable even when samples are excited with uv irradiation.[7] It should also be noted that in these post-irradiated samples, a peak at 401 nm in the electronic absorption spectrum is no longer observable.[5] This could be because in the now yellow-brown crystals it is overlapped by the tail of the intense band centered at 350 nm, or because it is entirely absent. Spectroscopic evidence indicates it to be absent.[5,8]

Thermoluminescence glow curves have also been obtained for freshly γ-irradiated specimens and post irradiated samples. Such a curve measures the intensity of total emission as a function of sample temperature as the specimen is heated. Thermal energy allows the trapped electrons to escape their traps and move about the crystal lattice and to eventually recombine with an ion giving luminescence. The deeper the electron traps, the more thermal energy required to release the electrons, and hence the glow curves as a function of temperature. The glow curves obtained on Hilton Deposit calcite are

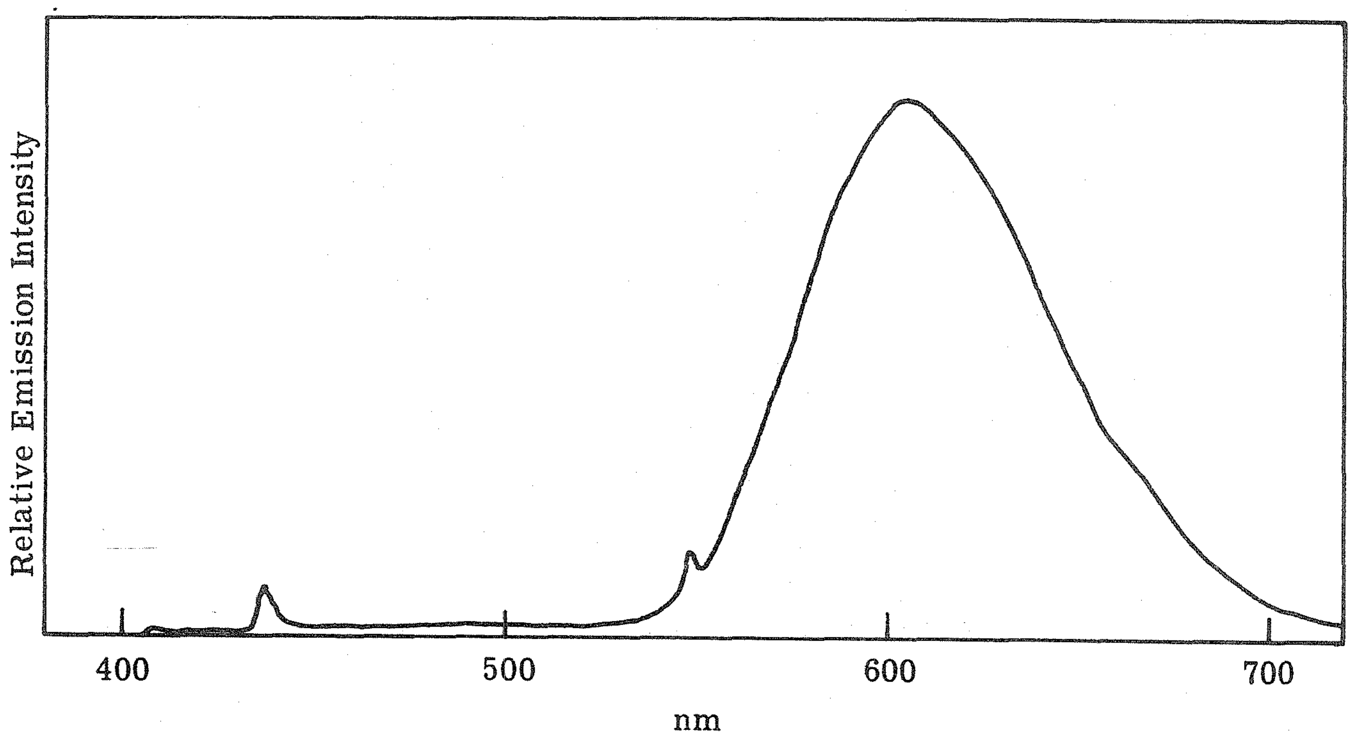

Figure 1. Cobalt-60 γ-ray radiation-induced room temperature emission spectrum of manganese containing calcite from the Hilton Deposit, San Diego County, California.

shown in Figure 2.[5] In the freshly irradiated sample, four luminescence events can be identified and they have their intensity maxima at 122, 178, 238, and 361 °C. The post-irradiated samples show maxima at 180, 230, and 360 °C. Presumably, the 122 °C trap is the site that slowly releases electrons and gives rise to the intense thermoluminescence immediately after γ-irradiation.

Electronic absorption and emission data strongly indicate that most, if not all, of the manganese in natural samples of Hilton Deposit calcite is in the +2 oxidation state. Presumably γ-irradiation induces loss of electrons from Mn^{2+} and leaves the ions in higher oxidation states. The thermal luminescence centered at 608 nm indicates that some Mn^{2+} is reformed as the irradiation damage heals. However, the lack of uv excited luminescence after storage of γ-irradiated samples suggest that only a very small percentage of the Mn^{2+} is reformed and persists, or that some secondary process occurs to deplete the Mn^{2+} as it is regenerated. The nature of the irradiation and post-irradiation processes is not known in sufficient detail to allow more than speculation on the fate of the Mn ions.

To better elucidate the processes that occur in these specimens, I now propose to carry out detailed and quantitative electronic absorption, emission, excitation, and electron spin resonance experiments on natural, γ-irradiated, and post-irradiated samples of Hilton Deposit calcite. It is extremely important that the experiments be quantitative so that an accurate determination of the percentage change in the

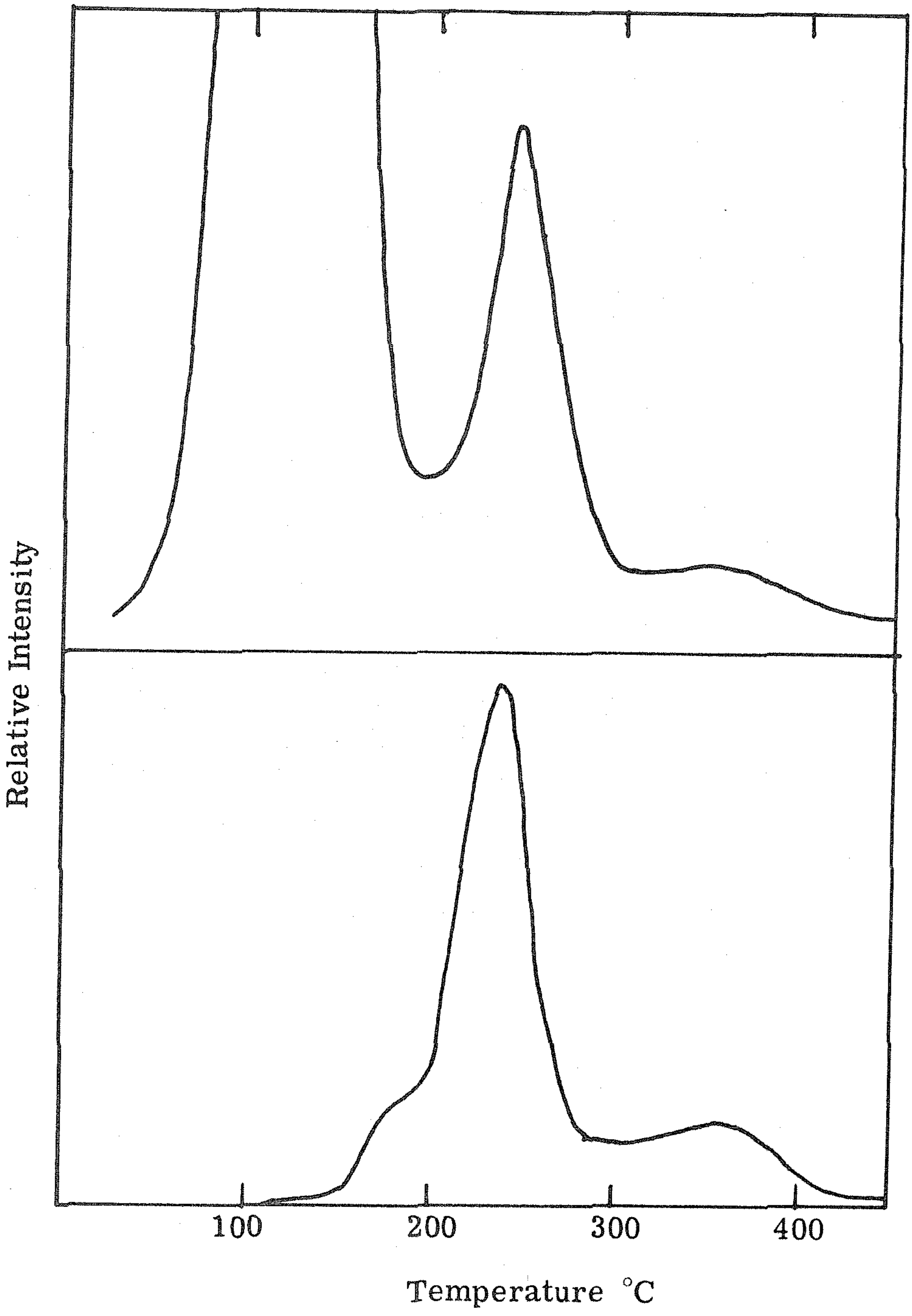

Figure 2. Thermoluminescence curve of manganese containing calcite from the Hilton Deposit, San Diego County, California. Top: luminescence allowed to decay 20 minutes after 10^6 rad dose; bottom: after being allowed to decay for two months after 10^6 rad.

nature of the Mn ions can be made. The electronic absorption studies should provide much information concerning the oxidation state of the manganese in the crystal. The +2, +3, and +4 states each have characteristic absorption bands (+2, ~401 nm[5]; +3, ~536 nm[9]; +4, ~630 and ~920 nm[9]). The ESR measurements should likewise give quantitative data concerning the fraction of Mn^{2+} in the crystal, and at low temperatures, possibly the amount of Mn^{3+} and Mn^{4+}. Quantitative emission and excitation spectra would also give information as to the percentage change in the Mn^{2+} concentration.

The following series of experiments are proposed. A finely powdered sample and a carefully cut and polished crystal (~ $\frac{1}{2}'' \times \frac{1}{2}'' \times \frac{1}{4}''$) of Hilton Deposit calcite should be prepared. The crystal should be firmly mounted on a sample holder that will allow the sample to be reproducibly positioned in electronic absorption and emission instruments. The electronic absorption, emission, and excitation spectra of the crystal should be measured, and the emission quantum yield determined. It would be advantageous to make measurements at both room temperature and at low temperatures. The ESR spectrum of the powdered sample should be measured, and the Mn^{2+} concentration should be estimated. The crystal and the powder should then be γ-irradiated for a period of time and then the same measurements should be repeated. It may not be possible to measure the room temperature absorption spectrum of the crystal because of the intense thermal luminescence. Of course, the excitation spectrum would also not be measurable.

Finally, the experiments should be repeated after the samples have been stored in the dark at 25 °C for about one month.

It would also be desirable to carry out the experiments on a sample of high Mn content calcite (~ 20-30%). This would be especially beneficial in the electronic absorption spectral studies as the absorption bands of the Mn^{2+}, Mn^{3+}, and Mn^{4+} ions would be better resolved. These samples should be γ-irradiated with the Hilton Deposit specimens so that accurate comparisons could be made. Finally, it would be desirable to repeat the entire series of experiments at various γ-irradiation times.

References

1. W. A. Deer, R. A. Howie, and J. Zussman, "An Introduction to the Rock-Forming Minerals," John Wiley and Sons, New York, 1966.
2. F. H. Pough and T. H. Rogers, Amer. Mineral., **32**, 31 (1947).
3. W. L. Brown, Univ. Toronto Studies, Geol. Ser. No. 36, 45 (1934).
4. F. H. Weber, County Report 3, Calif. Div. Mines and Geol., 52 (1963).
5. G. R. Rossman and D. D. Lawson, to be submitted.
6. K. L. Keester and W. B. Shite, Proc. Fifth Internat. Min. Assoc. Meet., Cambridge, England, 22 (1966).
7. G. R. Rossman and G. L. Geoffroy, unpublished observations.
8. G. R. Rossman, private communication.
9. G. R. Rossman and D. D. Lawson, to be submitted.

PROPOSITION IV

Photochemical Properties of Transition Metal Hydride Complexes

In Chapter II of this dissertation, it was shown that irradiation of some stable and "irreversible" dihydride complexes of Ir(III) results in reductive-elimination of molecular hydrogen and formation of coordinatively unsaturated Ir(I) species. Although the mechanism of this unique photochemical reaction was not fully elucidated, the reaction does suggest that other transition metal hydrides may behave similarly. I now propose to carry out an extensive investigation of the photochemical properties of a number of di- and polyhydride complexes with the hope of observing some very unusual reactions.

Photolysis of transition metal complexes with at least two hydride ligands can conceivably lead to three different types of reactions. The most probable reaction is simple reductive-elimination giving molecular hydrogen and a stable complex with the central metal in a lower oxidation state. Of course, this is the reaction observed for the iridium dihydrides, and such a reaction can occur only when two stable metal oxidation states differ by two electrons. Many of the hydride complexes which I propose to investigate should behave in this manner. One such series of complexes are the rhenium hydrides, $H_xRe(2\text{-phos})_2$ $(x = 3, 4, 5)$.[1] Irradiation of $H_5Re(2\text{-phos})_2$ should give the reaction shown in Eq. 1:

$$H_5Re(2\text{-phos})_2 \xrightarrow[\text{argon purge}]{h\nu} H_3Re(2\text{-phos})_2 + H_2 \qquad (1)$$

In these reactions it probably will be necessary to use an inert gas purge to remove the photoreleased H_2. Although the analogous $H_2Re(2\text{-phos})_2$ complex is not known,[1] irradiation of $H_4Re(2\text{-phos})_2$ could provide a convenient method of generating it. Another interesting application to rhenium hydrides would be the photolysis shown in Eq. 2:

$$H_5Re(2\text{-phos}) \xrightarrow[\text{argon purge}]{h\nu} H_3Re(2\text{-phos}) \qquad (2)$$

Irradiation of the known pentahydridomonophosphinerhenium complex could provide a convenient synthesis for the previously unknown trihydrido- species. Other complexes which should show this photoinduced reductive-elimination chemistry, giving a relatively stable product are listed below:

$H_5Re(PPh_3)_3$
$H_4ReBr(PPh_3)_3$
$H_7Re(PPh_3)_2$
$H_2RhCl(PPh_3)_2(py)$
$H_2Ir(acac)(PPh_3)_2$
$H_3IrCO(PPh_3)_2$
H_8RePPh_3
$H_7Re(AsEt_2Ph)_2$
$H_3Co(PEtPh_3)_2$
$H_2Rh(PPh_3)_2(NCCH_3)_2^+$
$H_3Ir(PPh_3)_3$
$H_5Ir(PPh_3)_2$

Although the products of the photolysis of these compounds are expected to be stable, some have not been previously reported.

It is also conceivable that photolysis of some hydride complexes could induce reductive-elimination leading to unstable and reactive products, which could subsequently undergo thermal reactions. These species could give very unusual chemistry. Although Ru(II) and Ru(0) are isoelectronic with Ir(III) and Ir(I), they differ in one important respect: Ru(0) does not form stable four-coordinate complexes whereas Ir(I) does. Thus if square-planar Ru(0) complexes can be generated, they are expected to be extremely reactive. One possible method of generating such species is via the photolysis of Ru(II) dihydrides. For example, irradiation of $H_2Ru(PPh_3)_4$[2,3] under an argon purge could give $Ru(PPh_3)_4$ (Eq. 3):

$$H_2Ru(PPh_3)_4 \xrightarrow{h\nu} Ru(PPh_3)_4 + H_2 \qquad (3)$$

Such a coordinatively unsaturated Ru(0) species is expected to immediately undergo a reaction to reach five or six coordination. If another ligand is not available, then the metal will probable insert into the ortho position of one of the phenyl rings of one of the phosphines, giving a 6-coordinate Ru(II) species. If the ortho-metalation can be prevented, possibly by chlorination of fluorination of the ortho positions of the rings, then the reactive Ru(0) complex might react with other species. Hopefully, one could observe insertion into a carbon-hydrogen bond of a solvent molecule, such as toluene or possibly hexane.

Although $H_2Mo(C_5H_5)_2$ and $H_2W(C_5H_5)_2$ are very stable compounds,[4] the related monomeric $M(C_5H_5)_2$ compounds have not been isolated.

However, polymeric forms with the general formula $[M(C_5H_5)_2]_x$[6] are known and permethylated dimers $\{M[C_5(CH_3)_5]_2\}_2$,[7] for both M = Mo and W have been prepared. Irradiation of solutions of these dihydrides under an inert gas purge could provide a very convenient synthesis of the $M(C_5H_5)_2$ species through a photo-induced reductive-elimination of molecular hydrogen. Even though the $M(C_5H_5)_2$ species might not be isolatable as solid compounds, they could be produced in solution.

Finally, a very interesting possibility is that irradiation of hydride complexes could induce hydride transfer to another coordinated ligand. Specifically, one might hope to observe hydride transfer to a coordinated dinitrogen ligand and observe reduction of the dinitrogen. Complexes which might show this photochemistry are $H_2Ru(N_2)(PPh_3)_3$,[7] $H_2Fe(N_2)(PEt_2Ph)_3$,[8] $H_2Fe(N_2)(PBuPh_2)_3$,[8] and $CoH(N_2)L_3$ (L = PEt_2Ph, $PEtPh_2$, PPh_3).[9] Since reductive-elimination is not desirable in this reaction, it probably would be necessary to irradiate solutions under an H_2/N_2 atmosphere.

References

1. H. D. Kaesz and R. B. Saillant, Chem. Rev., 72, 231 (1972).
2. T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda. J. Amer. Chem. Soc., 92, 3011 (1970).
3. A. Yamamoto, S. Kitazume, and S. Ikeda, J. Amer. Chem. Soc., 90, 1089 (1968).
4. M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, J. Chem. Soc., 4854 (1961).
5. J. L. Thomas and H. H. Brintzinger, J. Amer. Chem. Soc., 94, 1386 (1972).
6. J. L. Thomas, J. Amer. Chem. Soc., 95, 1838 (1973).
7. A. Sacco and M. Rossi, Chem. Commun., 316 (1967).
8. A. Sacco and M. Aresta, Chem. Commun., 1223 (1968).
9. A. Sacco and M. Rossi, Inorg. Chim. Acta, 2, 127 (1968).

PROPOSITION V

Electron Impact Spectra of Organometallic Molecules Using Ion Cyclotron Resonance Spectroscopy

Ion cyclotron resonance spectroscopy has recently been shown to be a very useful technique for obtaining electron impact spectra of chemical species.[1-3] When an energetic electron interacts with a ground state molecule, it can transfer some or all of its energy to the molecule, producing electronically excited states. The quantum condition must be obeyed in such energy transfer, and as a consequence of the transfer, the electron loses part of its translational energy. If the initial energy of the electron is exactly equal to the energy difference between the ground state and some excited state of the molecule, then after energy transfer, the electron will be left with zero energy.

Low energy electrons can be trapped in the ICR spectrometer by application of a negative potential to the trapping electrodes, thereby creating an effective potential well for the electrons.[1] The parabolic potential well between the electrodes has been shown to have a depth of approximately half the applied voltage, and the residence time of electrons in the well can approach 0.1 sec.[1] Thus low energy electrons generated by impact excitation of a molecule can be trapped if their final translational energy is less than the depth of the potential well. Such trapped electrons cannot be detected in conventional ICR spectrometers because of their high cyclotron resonance frequency. However, they can be indirectly detected by allowing them to induce a chemical reaction whose products are detectable. For example, the reaction in Eq. 1:

$$e^- + CCl_4 \rightarrow Cl^- + CCl_3 \qquad (1)$$

occurs and has been shown to have a cross-section of 160 Å^2 for zero energy electrons.[4]

The usual technique for obtaining electron impact spectra in an ICR spectrometer is to adjust the well depth to about 0.2 eV and then scan the electron energy in the presence of the sample and about 0.1% CCl_4.[1,3] The Cl^- produced is monitored and a plot of its resonance intensity versus electron energy gives the excitation spectrum of the sample. An example of such a spectrum obtained for N_2 is shown in Figure 1.[1] In addition to CCl_4, $C_2H_5NO_2$[5] and SF_6[6] have been employed as electron scavengers and McAllister[2] has presented a direct method for detection of low energy electrons.

I now propose to apply this technique for obtaining electronic excitation spectra to various organometallic species. The real promise of this technique lies in the relaxation of spin-selection rules by threshold energy electron impact, producing both spin-allowed and spin-forbidden transitions with high probability.[7] Thus in selected organometallic species it should be possible to indentify spin-forbidden transitions that have not been observable by conventional spectroscopic techniques. The only requirement for the complexes to be studied is that they be sublimable at temperatures attainable in a heated inlet port.

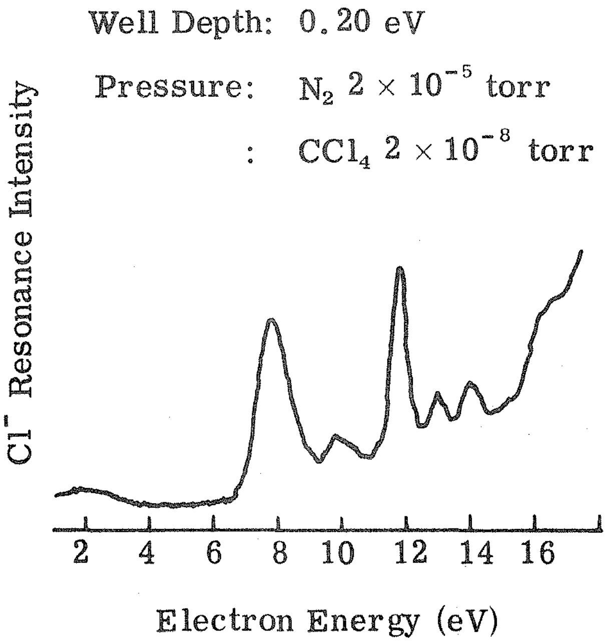

Figure 1. Inelastic excitation spectrum of N_2 obtained by scavenging trapped low-energy electrons with CCl_4 and measuring the resultant Cl^- with ion cyclotron resonance spectroscopy.

Probably the most important species that can be studied using this technique is ferrocene. The location of the ligand field triplet states in this molecule has been the subject of numerous papers and is still a much debated subject.[8-14] Scott and Becker[8,9] claimed to observe three spin-forbidden transitions at 14.2 kcm^{-1} ($\epsilon = 0.16$), 16.1 kcm^{-1} ($\epsilon = 0.34$), and 18,59 kcm^{-1} ($\epsilon = 8$) which they assigned to $^1A_{1g} \rightarrow {}^3E_{1g}$, $^1A_{1g} \rightarrow {}^3E_{2g}$, and $^1A_{1g} \rightarrow {}^3E_{1g}$, respectively. They also observed a long-lived ($\tau = 2$ sec) phosphorescence centered at 17.5 kcm^{-1} which they attributed to $^3E_{1g} \rightarrow {}^1A_{1g}$.[8] McGlynn and coworkers[10] observed similar absorption transitions but were unable to detect any phosphorescence. However, Smith and Meyer[11] observed a long-lived ($\tau = 0.5$ sec) luminescence centered at 20.0 kcm^{-1} in a frozen methane matrix, but did not observe the low intensity absorption bands. Recent workers[12,13] have failed to detect any long-lived phosphorescence from ferrocene, even with very intense laser excitation (10^{24} photons/sec), and it now appears that previous observations must be abscribable to impurities. Recent detailed spectroscopic measurements by Gray, et al.,[14] have led to the conclusion that the 18.59 kcm^{-1} band observed by Scott and Becker is the only band which can be attributed to a ligand field singlet-triplet transition. A ligand field theory analysis of the absorption spectrum of ferrocene, based on the position of the observed spin-allowed transitions and an assumed C/B ratio of 4.0, has led to the calculated positions of the spin-forbidden transitions as 22.4, 20.9, and 18.6 kcm^{-1} for $^1A_{1g} \rightarrow b\,{}^3E_{1g}$, $^1A_{1g} \rightarrow {}^3E_{2g}$, and $^1A_{1g} \rightarrow a\,{}^3E_{1g}$, respectively.[14] Clearly, an electron impact excitation study using the ICR method, in which the singlet-triplet transitions should be observable, would be extremely valuable in resolving this controversy. I propose to carry out this experiment.

There are many other organometallic species which should be investigated using this technique. These include $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ for which it would be very interesting to try to find a low energy singlet-triplet transition analogous to that observed in the absorption spectrum of $W(CO)_5L$ species.[15] It would also be interesting to study the substituted manganese carbonyls, $Mn(CO)_5X$ ($X = Cl^-$, Br^-) whose electronic absorption spectra have also been much discussed in recent years.[16-18]

References

1. D. P. Ridge and J. L. Beauchamp, *J. Chem. Phys.*, **51**, 470 (1969).
2. T. McAllister, *Chem. Phys. Lett.*, **13**, 602 (1972).
3. O. A. Mosher, M. S. Foster, W. M. Flicker, J. L. Beauchamp, and A. Kuppermann, to be submitted.
4. C. E. Brion and G. E. Thomas, *Intern. J. Mass. Spectry. Ion Phys.*, **1**, 25 (1968).
5. P. Kriemler and S. E. Buttrill, *J. Amer. Chem. Soc.*, **92**, 1123 (1970
6. R. M. O'Malley and K. R. Jennings, *Intern. J. Mass. Spectry. Ion Phys.*, **2**, App 1-3 (1969).
7. G. J. Schultz, *Phys. Rev.*, **116**, 1141 (1959).
8. D. R. Scott and R. S. Becker, *J. Organomet. Chem.*, **4**, 409 (1965).
9. D. R. Scott and R. S. Becker, *J. Chem. Phys.*, **35**, 516 (1961).
10. A. T. Armstrong, F. Smith, E. Elder, and S. P. McGlynn, *J. Chem. Phys.*, **46**, 4321 (1967).
11. J. J. Smith and B. Meyer, *J. Chem. Phys.*, **48**, 5436 (1968).
12. A. Müller-Goldegg and J. Voitländer, *Z. Naturforsch.*, **23A**, 1236 (1968).
13. R. Schandry and J. Voitländer, *Z. Naturforsch.*, **26A**, 1772 (1971).
14. Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 3603 (1971).
15. M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 4336 (1971).
16. H. B. Gray, E. Billig, A. Wojcicki, and M. Farona, *Can. J. Chem.*, **41**, 1281 (1963).

17. G. B. Blakney and W. F. Allen, Inorg. Chem., **10**, 2763 (1971).

18. S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard, and D. W. Turner, Discuss. Faraday Soc., **No. 47**, 112 (1969).